TEXTILE RESEARCH JOURNAL

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T. R. I. Annual Meeting

THE TWENTY-FOURTH ANNUAL MEETING of Textile Research Institute will be held in the Main Ballroom, Hotel Commodore, New York City, on Thursday and Friday, November 12 and 13, 1953. The program for the meeting follows.

General Chairman: T. G. Hawley, Jr., Director of Research, United Merchants Laboratories, Inc.

Thursday, November 12

9:00 A.M.—Registration

10:00 A.M.—Morning Session (*Chairman:* Hawley)

"Results of Institute Research in 1953," by James H. Wakelin, T.R.I.

"Ten Thousand and One Consumer Complaints and Their Implications for Textile Research and Development," by Jules Labarthe, Mellon Institute of Industrial Research

12:45 P.M.—Luncheon Session

Introduction of Officers, etc., by D. H. Powers, Director of Research, Warner-Hadnut, Inc.

The State of the Institute, by J. H. Dillon, Director, T.R.I.

2:15 P.M.—Afternoon Session (*Chairman:* L. Smith)

"Some Chemical Experiments on Wool," by Harold P. Lundgren, Western Regional Research Laboratory

"Optical and Electron Microscopic Studies of Cotton Fiber Structure," by Mary L. Rollins, Southern Regional Research Laboratory

"Production and Properties of Spun-dyed Acetate," by George Wernz, Tennessee Eastman Co.

Friday, November 13

Symposium on Fiber Blends

10:00 A.M.—Morning Session (*Chairman:* Setterstrom)

"Complementary Functions of Natural and Synthesized Fibers in Fabrics," by J. B. Quig, E. I. du Pont de Nemours & Company, Inc.

"Problems in Fiber Blends," by J. B. Goldberg, consultant

12:30 P.M.—Luncheon

2:00 P.M.—Afternoon Session (*Chairman:* Woodruff)

"Some Problems of Blend Fabrics," by Milton Harris, Harris Research Laboratories

"Finishing of Blends," by Hector Borghetty, Rohm & Haas Company

"Progress in the Dyeing of the Newer Synthetic Fibers," by Paul Choquette, General Dyestuffs Corporation

4:15 P.M.—General Discussion (*Chairman:* Hamburger)

Exhibits, West Ballroom

Instruments, Fibers, and Chemicals

TEXTILE RESEARCH JOURNAL

VOL. XXIII, NO. 10 October, 1953

Fundamentals of the Dyeing of Cellulosic Fibers*

H. R. McCleary

Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey

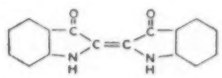
Introduction

The annual production of coal-tar dyes in the United States amounts to approximately 150,000,000 lbs., of which about 60% is used for cellulosic fibers. The two dye types making up most of this 60% are the *direct* dyes and the *vat* dyes. The large majority of direct dyes are organic azo sulfonic acid salts which are water-soluble and which have marked affinity for cellulose. An example is Chrysophenine G, a yellow dye which is a derivative of stilbene, containing two sulfonic acid groups and two azo groups. The linear structure of this dye is typical of the direct dyes. If a 10-g. sample of cellulosic material is immersed in 500 ml. of a dilute aqueous solution of a direct dye containing added electrolyte at 50° to 100°C, the dye, as a colored anion, will be exhausted more or less rapidly onto the cellulose, causing the solution to lose much of its color. This property of a dye to be preferentially absorbed is called "substantivity." It is obvious that substantivity is a unique property of dyes, since many colored compounds have no substantivity.

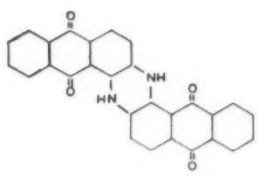
The vat dyes are water-insoluble compounds based historically on indigo, although a great many dyes in this class are derivatives of anthraquinone and related compounds. Examples shown in Figure 1 are indigo and indanthrone, an anthraquinone vat blue. The common feature of all vat dyes is that they contain carbonyl groups which may be reduced in alkaline solution yielding the soluble alkali salts of corresponding hydroxyl derivatives—the leuco compounds. When cellulosic materials are immersed in these "sodium leuco" solutions, the leuco dye, as an anion, is absorbed in much the same manner as the direct dyes, and is therefore "substantive." Oxidation of the leuco in cellulose gives back the insoluble pigment form of the vat dye, which is "trapped" within the cellulose structure, and which is therefore very fast to washing.

The mechanism by which dyes transfer from solution to fiber, the factors which control the rate and equilibrium value in dyeing, and the reasons for substantivity have been subjects of much investigation for several years. Some excellent surveys of this subject have appeared, among which may be mentioned the book by Vickerstaff [26]. It is the purpose of the present paper to cover the more important principles in the dyeing of cellulosic materials.

The nature of the substrate, cellulose, and the



INDIGO



INDANTHRONE

FIG. 1

* Presented before the Division of Cellulose Chemistry, American Chemical Society, New York, Sept. 1951.

properties of dyes and dye solutions will be considered briefly before discussing the dyeing process itself.

The Substrate—Cellulose

As a chemical substance, cellulose is a polymer of glucose, the repetitive unit, cellobiose, being composed of two glucose units. The length of the cellobiose unit is 10.3 Å., which is believed to be important in relation to the dimensions of substantive dye molecules, as will be discussed later.

The examination of a single fiber of natural cellulose, such as cotton, shows it to be composed of a very thin primary wall surrounding a multilayer secondary structure in the center of which is a central canal or lumen which collapses when the initially "green" fiber dries. These primary and secondary structures are the substance of dried cotton fibers, which are made up of spirally wound "fibrils" of cellulose which are submicroscopic in size. The fibrils, in turn, are made up, so to speak, of "bundles" and "tangled brush heaps" of linear polymeric cellobiose chains. Neatly arranged "bundles" may be regarded as the crystalline portions or "crystallites" of cellulose, while the "brush heaps" are the amorphous or intercrystalline regions. The degree of crystallinity varies, depending on the source of the fiber. One of the most crystalline is the natural fiber ramie, while certain types of regenerated cellulose are among the least crystalline types. The regenerated cellulose fibers do not have the primary and secondary structures characteristic of natural cellulose fibers, but they frequently do have "skin" structures which alter their properties.

The linear cellobiose polymer "molecules" have degrees of polymerization varying from about 300 glucose units per chain for some types of regenerated cellulose to an average of 2,000 units per chain for natural cellulose. A single chain may thus be a part of several crystallites, running in snake-like fashion from one crystallite to another and giving rise in between to the amorphous, intercrystalline regions.

By virtue of the three hydroxyl groups per glucose unit, cellulose is a hydrophylic substance and is readily wet by water. It swells on immersing in water, the increase in size of a fiber being due largely to sorption of water by the amorphous regions. The water, in a sense, surrounds the cellobiose chains. In dyeing, this makes possible the approach of dye molecules to the surface of the chains where they may become attached. If this picture is correct, the total available surface area of the amorphous regions is therefore important in considering the phenomenon of dyeing. Hunt, Blaine, and Rowen [11] reported a surface area of 71 m.²/g. from nitrogen sorption measurements on caustic-swollen and solvent-dried cotton linters. These authors calculated from these data a "pore size" of 20 Å for caustic-swollen cotton and 16 Å. for water-swollen cotton. These values are somewhat lower than values of 40 Å or more reported by Valko [25] in his review of earlier determinations. In so far as a calculated pore size is a reality, it is important in considering the take-up of dyes, since the single dye molecule must obviously be smaller than the pores in order to diffuse through cellulose.

Dyes and Dye Solutions

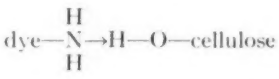
The properties which a colored substance must have in order for it to be a cellulose dye are not easily defined. A simple experimental test of a soluble colored substance is to prepare an aqueous solution of the color, under conditions normally regarded as optimum for dyeing, and immerse therein a skein of cellulose yarn. If the concentration of color in the solution decreases appreciably due to sorption of the color by the cellulose, the color is a dye and is said to possess "substantivity." Dyes may have high or low substantivity and may vary considerably in their fastness properties when dyed samples are rinsed repeatedly in distilled water.

Vickerstaff [26] reviewed the work of many investigators who studied the relationship between chemical structure and substantivity, and summarized the following requirements which should be fulfilled in order for a dye to be substantive to cellulose: "(*1*) The molecule should be capable of assuming a linear configuration. (*2*) The aromatic nuclei should be capable of assuming a coplanar arrangement. (*3*) The molecule should contain groups capable of forming hydrogen bonds. Favorable, but not essential, conditions are: (*4*) The presence of a conjugated system of double bonds, which by resonance promotes coplanarity of the molecule and probably favours hydrogen bond formation by the groups at the ends of the conjugated chain. (*5*) Widely spaced hydrogen bond-forming groups, spaced at a distance corresponding as nearly as possible to the cellulose unit length of 10.3 Å. or some multiple of this distance. (*6*) The presence of the minimum number of solubilising groups necessary for solubility. (*7*) The disposition of the solubilising groups along one side

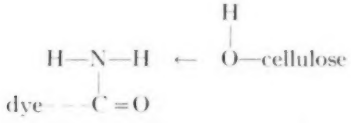
of the dye molecule and of hydrogen bonding groups along the other side."

Marshall and Peters [12] cited the two isomeric disazo dyes shown in Figure 2 as examples of the effect of linear structure on substantivity. The linear chainlike structure of the first compound, a direct red dye, permits the molecule to lie close to the cellobiose chain and to be held there by residual valence forces. The nonlinear form of the isomeric compound does not fit conveniently onto cellulosic chains, and it has poor substantivity.

The hydrogen bonding which is believed to hold dye molecules onto cellulose undoubtedly occurs with the hydroxyl groups of cellulose. Such bonding may occur with either electron-donating or electron-accepting groups on the dye molecule. For example, an amino group on the dye would provide the bonding electrons



while in the case of an amide group the bonding electrons might be furnished by the cellulosic oxygen



The properties of dyes in aqueous solutions are important in a consideration of dyeing, since, in general, dyes are applied from aqueous solutions. Although there are some exceptions, the aggregation of most direct dyes in water solution is, perhaps, a characteristic feature of this class. The degree of aggregation varies widely depending on the dye, the temperature, electrolyte concentration, and certain other factors. The presence of hydrogen-bonding groups on direct dyes is probably responsible for intermolecular aggregation. Valko [25] pointed out that the residual valence forces which are responsible for substantivity of a dye for cellulose are probably the same as those which cause aggregation. The addition of salt to a dye bath increases both the exhaustion of dye onto cellulose and the degree of aggregation of the dye in solution. This is due to the effect of the electrolyte in lowering the electrostatic force of repulsion between a dye anion and negatively charged cellulose in the case of dyeing, and between two or more dye anions in the case of aggregation. Because of the parallelism between dye aggregation and dye exhaustion on the addition of salt to a dye bath, an older theory of dyeing regarded dye exhaustion as a "salting out" of dye onto cellulose, purely as a result of decreased solubility. We now believe that the presence of salt in direct dye solutions causes dye exhaustion to take place in spite of aggregation and not because of it.

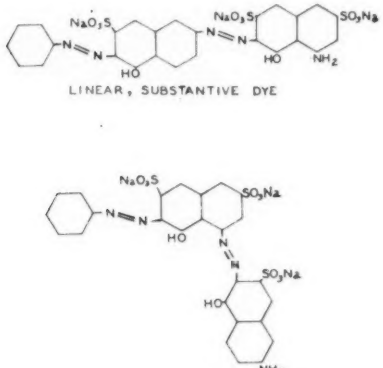


FIG. 2. *Effect of structure on the substantivity of direct dyes.*

A mixture of two direct dyes in aqueous solution frequently has a color which is not that expected from the individual colors—that is, the spectrophotometric curves of the two dyes are not additive. This is probably due to intermolecular association between the molecules of two different species causing a mutual interaction which changes the absorption spectrum of each dye. Taylor and Simon [24] and, more recently, Martin and Standing [13] showed that the addition of certain polyethylene oxide condensates to dye mixtures causes the spectrophotometric curve to be the additive sum of the curves of the individual dyes in solution with the condensate. The condensate is believed to associate with each dye and to prevent intermolecular association between dyes. As might be expected, the dyeing properties of a dye solution are usually affected by the addition of a condensate to the dye bath. In a sense, the condensate competes with the cellulose for association with the dye and more dye is left in solution at dyeing equilibrium.

The nonaggregating properties of the simple azo acid dyes for wool are in agreement with these views on direct dyes. The simple acid dyes have affinity for

wool by virtue of their sulfonic acid groups. Therefore, they do not need to be large molecules of unique structure which provide hydrogen-bonding groups for linkage to the wool fibers. Without such uniformly spaced bonding groups, the simple acid dyes have much less tendency to aggregate in solution, and their spectrophotometric curves are generally additive.

Vat dyes in leuco form are believed to have affinity for cellulose for much the same reasons as direct dyes, and might therefore be expected to aggregate in solution. Recently, however, Fowler, Michie, and Vickerstaff [8] made an extensive equilibrium dyeing study for several vat dyes on cotton yarn, and found that the vat dyes in leuco form at 40°C are not aggregated to any considerable extent in spite of the high concentration of electrolyte in vat leuco solutions. There are a few direct dyes which do not aggregate in solution at room temperature because of certain structural considerations; the same principles may apply more generally to many vat dyes because of mutual repulsion of the phenolate groups of reduced anthraquinone rings, thus preventing aggregation.

The Dyeing Process

Two important aspects of dyeing—rate and equilibrium—are evident from Figure 3, in which curves are given for rayon skeins dyed at two different temperatures, 50° and 90°C [23]. A commercial direct dye, Sky Blue FF (Colour Index No. 518), was used in a 400-cc. dye bath containing 1.0 g. NaCl. Viscose rayon skeins weighing 10 g. were stirred in the thermostated dye baths, and spectrophotometric measurements were made on the solutions at various times in order to determine the "% dye bath strength." Plots of these data give "exhaustion" curves which show the magnitude of the increase in exhaustion rate with increase in temperature. An increase in temperature causes a decrease in the equilibrium amount of dye transferred to the fiber. This means that the reaction

$$\text{dye (solution)} \longrightarrow \text{dye (cellulose)}$$

is exothermic, and ΔH for the reaction is therefore negative. These same effects are found in the dyeing of the vat dye leucos onto cellulose.

The effect of electrolyte concentration in the dyeing of direct dyes [23] is shown by Figure 4. The dyeings were made with Sky Blue FF on 10-g. viscose rayon skeins in dye baths containing amounts of NaCl varying from 0.5 to 10 g. per 400 cc. Both the rate of dyeing and the equilibrium dye absorption are increased by increase of salt concentration. This effect is much less evident in the dyeing of vat leucos because of the high initial electrolyte concentration which is necessary in preparing the leuco solution.

Rate of Dyeing

From a practical point of view, the rate of removal of dye from a dye bath by a fiber or fabric is very important. This rate of "exhaustion" must be high enough to make the process economical. On the other hand, the rate must not be so high as to prevent uniform dyeing of the substrate. At high exhaustion rates the portions of the material which first touch the dye bath become darkly dyed, leaving other portions only lightly dyed. At equilibrium these differences in depth of color usually level out, but this may require an impractically long time.

One of the factors determining the rate of exhaustion of dye from solution is the stirring rate—the effectiveness with which the fiber and solution are agitated with respect to each other. Alexander and

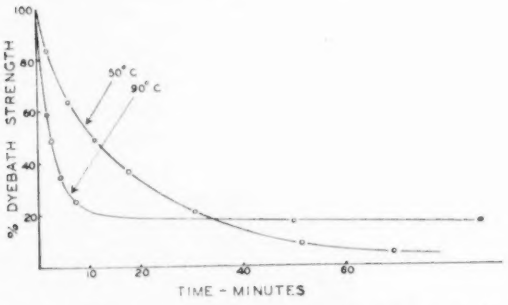


FIG. 3. *Effect of temperature on the dyeing of Sky Blue FF on viscose rayon.*

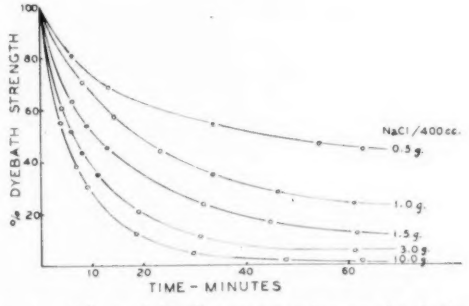


FIG. 4. *Effect of NaCl concentration on the dyeing of Sky Blue FF on viscose rayon.*

Hudson [1] in some studies of wool dyeing measured the temperature effect on the rate of dyeing at different stirring rates. They found a sharp change in the activation energy of dyeing from 5 to 13 kg.-cal./mole as the stirring rate was increased. At lower stirring rates, the dyeing rate was controlled by diffusion of dye through the stagnant solution layer surrounding the individual fibers. At higher stirring rates, diffusion of dye within the fiber was rate-controlling.

The mechanism by which a cellulose dye is exhausted from solution and transferred onto and through a fiber of cellulose is best understood by the following simplified picture of dyeing. Let a fiber be immersed into a large dye bath so that during dyeing there will be essentially no change in the bath concentration. Almost immediately after immersion of the fiber, dyeing of an infinitesimally thin surface portion of the fiber takes place, with establishment of an equilibrium between the concentration of dye in this layer and the concentration in solution. Dyeing then proceeds by diffusion of dye from this surface region towards the center of the fiber until the fiber is uniformly dyed throughout. Dyeings in which the bath is of finite size are more complex because the concentration of dye in the fiber surface is continually decreasing during dyeing in order to maintain equilibruim with the exhausting dye bath. This situation complicates the systematic interpretation of data, but does not change the picture of the process.

Crank [5] made a thorough study of the diffusion of direct dyes into cellulose from a theoretical point of view. Experimental methods for the determination of diffusion coefficients of dyes in cellulose have included (*a*) dyeing of Cellophane in an infinitely large-volume dye bath and (*b*) dyeing of cylindrical fibers in an infinite bath. The mathematics of the second method are more complex than the first. Crank has worked out the mathematics for a third experimental method—the dyeing of cylindrical fibers in a finite-volume bath. This involves correction for the exhausting dye bath and makes the method for determining diffusion coefficients comparable to practical dyeing methods.

There have been two principal pictures of the mechanism of cellulosic dyeing expressed by various investigators. The first picture regards the intercrystalline regions of water-swollen cellulose as being made up of semipermanent capillaries or pores filled with water, through which dye molecules may diffuse and become attached to cellulose chains along the walls.

The second picture regards swollen cellulose as a matrix of chains knotted together at random points to form "crystallites," the intercrystalline regions being filled with a viscous solution of flexing cellulose chains in water. Dye ions diffuse through this solution and become attached to the chains.

The latter picture of dyeing is generally preferred. Crank pointed out that the pore theory of dyeing is oversimplified and that pore diameters of 20–30 A. calculated according to this theory cannot be reconciled with the diffusion behavior of many dyes of comparable molecular size.

A simplified view of the diffusion of dye within cellulose is to regard it as free diffusion in water modified by the following factors: (*1*) the hindrance of the network of cellulose chains which get in the way of diffusing dye molecules; (*2*) the affinity of cellulose for dye; this causes dye molecules, which otherwise might have diffused farther, to attach themselves to cellulose chains; (*3*) the hindrance of diffusion because of electrical repulsive forces between diffusing dye anions and cellulose chains, which are negatively charged due to carboxyl groups and/or adsorbed dye anions.

The temperature coefficient of diffusion of dye within cellulose fibers is considerably higher than that for simple water diffusion. Thus, for a certain red dye in the presence of a given NaCl concentration, Crank reported that "the ratio of the apparent diffusion coefficients at 90°C and 25°C respectively is about 64, compared with a corresponding ratio of about 4 for the aqueous diffusion coefficients." It is pointed out that the 25°C data may be complicated by some dye aggregation. The large temperature coefficient of diffusion in fibers is nevertheless real, and is largely due to the fact that the affinity of cellulose for dye decreases with increase in temperature.

The effect of salt concentration on dyeing rate, shown graphically in Figure 4, is reported in Table I, in which the initial slope of the exhaustion curve is listed for each salt concentration. This zero-time slope is designated "initial exhaustion rate" [23], and is expressed as the percentage of the initial dye

TABLE I. EFFECT OF NaCl CONCENTRATION ON INITIAL EXHAUSTION RATE

NaCl concentration (g./l.)	1.25	2.5	5.0	12.5	25.0
Initial exhaustion rate (%/min.)	3	6½	10½	17	22

concentration exhausted per minute. These are for dyeings of Sky Blue FF on viscose rayon skeins at 90°C under practical dyeing conditions.

More fundamental studies by Neale [16] and others of the effect of salt on dyeing show the striking effect of salt concentration on the apparent diffusion coefficient, D, of dye in cellulose. As shown in Figure 5 for Benzopurpurine 4B, D increases very rapidly at low concentrations, and then passes through a maximum with further increases in salt. The experimental points are those of Neale, while the continuous curve was calculated by Crank. Excellent agreement between experiment and theory is apparent.

Two effects may be noted here: (*1*) With no salt there is virtually no diffusion. This is due to the electrical repulsion of negatively charged cellulose and dye anions. Addition of small amounts of salt rapidly lowers this potential barrier, permitting a sharp increase in diffusion. (*2*) The diffusion coefficient passes through a maximum. This is due to the increasing adsorption of dye anions by cellulose chains with increasing salt concentration and possibly to other factors such as aggregation.

Crank pointed out that a complete understanding of dye diffusion in cellulose is not possible without further experimental work directed towards certain aspects of the problem.

A final point about rate of dyeing is the large range of diffusion rates among direct dyes. Boulton [3] measured the "times-of-half-dyeing" for a long list of direct dyes, and found them to vary over a range of 1 to 3,700. This half-dyeing value is closely related to diffusion rate because of the special conditions used for carrying out the dyeings. In dye houses of the textile industry, dye mixtures, rather than single dyes, are most often used to match a shade. Boulton emphasized the desirability of choosing dyes which have similar diffusion rates in order to obtain uniformity of shade and strength on the dyed material.

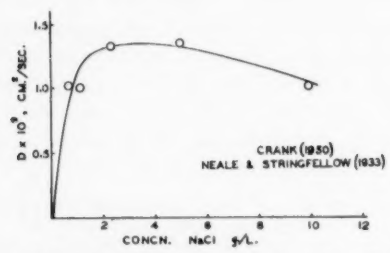


FIG. 5. *Apparent diffusion coefficient for Benzopurpurine 4B in Cellophane.*

A committee of the Society of Dyers and Colourists in England made a survey of a large number of direct dyes [2], and divided them into three classes—namely, (*a*) "self-leveling," (*b*) "salt-controllable," and (*c*) "temperature-controllable." These classifications refer to dyeing behavior of the dyes, and the descriptive terms indicate the variable which must be controlled in order to obtain uniform dyeings on cellulosic materials. Such classifications are useful to the practical dyer in choosing dyes and dyeing procedures.

Equilibrium in Dyeing

Studies of the thermodynamics of dyeing have provided the basis for various theories of dyeing which have been advanced in recent years. No attempt will be made to review all of this work, but typical experiments will be cited.

It is well known that dyeing is an equilibrium phenomenon, since nearly all the dye can be removed from direct-dyed cotton by repeated rinsing in water. The effect of temperature on equilibrium was measured by Graham and Fromm [9] for dyeings of Blue 4GL (C.I. 533) on cotton from solutions containing 4.0 g./l. of sodium chloride. Figure 6 shows log-log plots of sorption isotherms for three temperatures. When values of log dye concentration, read along the dashed lines at constant concentration of dye in fiber, were plotted against the reciprocal of absolute temperature, the straight-line plots shown in Figure 7 were obtained. The slopes of these plots give the ΔH values for the exothermic dyeing reaction. Table II shows that $-\Delta H$ increases with decrease in equilibrium dye sorption.

Graham and Fromm proposed, as an explanation of this variation of ΔH, that the sorption affinity of

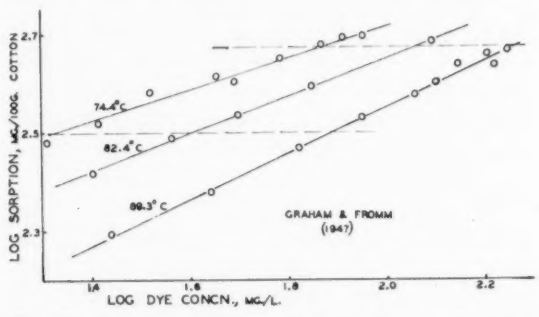


FIG. 6. *Sorption isotherms for the dyeing of cotton with direct Blue 4GL.*

cellulose for dye is nonuniform since cellulose itself is not completely homogeneous. The portions of the cellulose which are most active will be the portions which take up dye first, and the less active portions then become dyed. The heat of dyeing would be expected to be greatest for sorption on the most active portions of cellulose, and therefore greatest at lowest sorption values. As pointed out by Graham and Fromm, this is consistent with the fact that in a solvent-extraction procedure used to remove dye from cotton, a major portion of the dye was readily removed while removal of the remainder of the dye required prolonged extraction.

A practical aspect of the effect of temperature on dyeing equilibrium is shown by a typical exhaustion curve in Figure 8. In this dyeing the temperature was held constant until the bath came almost to its equilibrium value; then the temperature was lowered, causing further exhaustion of dye from the bath. Dyers often utilize this principle by lowering the temperature of the bath near the end of dyeing in order to obtain darker dyeings.

The effect of salt on the equilibrium exhaustion of a dye onto cellulose was referred to earlier. Since equilibrium exhaustion increases with increasing salt concentration, it is apparent that some saturation value for dye on cellulose will be reached eventually.

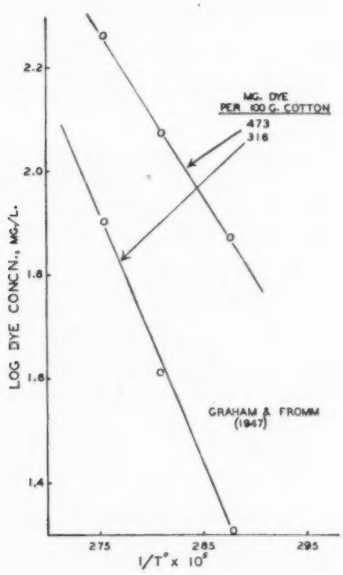


FIG. 7. *Dyeing equilibrium* vs. *temperature for the dyeing of cotton with direct Blue 4GL.*

Neale and Stringfellow [17], in experiments made to determine the saturation value of cotton, obtained results which were not conclusive, but they calculated from their most reasonable saturation value that the total surface area occupied by dye molecules lying flat was 150 m.²/g. cotton. Considering the nature of these experiments, this is not in serious disagreement with the value of 71 m.²/g. for the internal surface of caustic-swollen cotton linters reported by Hunt, Blaine, and Rowen [11] from nitrogen sorption measurements. The dye saturation value was high probably because of dye aggregation within the fiber, especially since the salt concentration of the dye bath was very high—100 g./l.

The theoretical aspects of the effect of salt and of temperature on direct-dyeing equilibrium have been considered by a number of investigators, prominent among whom are Neale and his coworkers, Standing and his coworkers [27], Crank [4], and Peters and Vickerstaff [18]. One of the most successful approaches is the thermodynamic treatment of Peters and Vickerstaff, which was applied to a number of dyes by Marshall and Peters [12]. The standard free energy change in dyeing was expressed as RT times the logarithm of the ratio of activities of dye in fiber and in solution. The activity of dye in the fiber was taken as the product of its ion concentrations, each divided by an "effective volume," V, of the cel-

TABLE II. HEAT OF DYEING AT VARIOUS EQUILIBRIUM SORPTION VALUES

Sorption (mg. dye/100 g. cotton)	$-\Delta H$ (kg. = cal./mole dye sorbed)
473	15.2
422	17.1
383	18.8
355	20.3
316	22.4

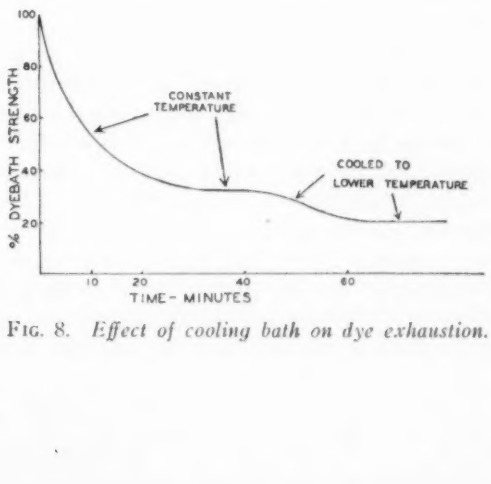


FIG. 8. *Effect of cooling bath on dye exhaustion.*

lulose. The Donnan membrane equilibrium was assumed to hold. It was then possible to calculate the concentration of sodium ions in the fiber from the analyzed concentration of dye anions in the fiber and the known concentrations of both dye and salt in solution. Knowing all these concentrations, it was possible to calculate directly the standard free energy change from any set of equilibrium dyeing data. Two important features of these calculations are: *(1)* The sodium ion concentration in the fiber is *not* assumed to be simply that associated with dye anions; thus the concentration of salt within the fiber is not neglected. *(2)* There is some controversy as to the physical significance of V, the "effective volume" of cellulose. It must be determined by dye adsorption experiments. It appears to be related to the effective volume of solvent water within the swollen cellulose phase.

Marshall and Peters obtained data from over 100 isotherms using fourteen direct dyes on four types of cellulose—namely, cuprammonium and viscose rayons, cotton, and mercerized cotton. According to the theory of Peters and Vickerstaff, a plot of log activity-of-dye in cellulose *versus* log activity-of-dye in solution should give a straight line of unit slope. Using this test, Marshall and Peters found that for six of the fourteen dyes which they studied, there was good agreement between theory and experimental results at dyeing temperatures from 60° to 90°C. Five more of the dyes showed agreement with theory at 90°C, while the remaining three dyes did not agree with theory at any temperature. These deviations were attributed to aggregation of certain dyes at lower dyeing temperatures. The free energies of dyeing, representing the dye affinities for various dyes, ranged from 2.8 to 6.3 kg.-cal./mole at 90°C. The heats of dyeing calculated from reciprocal-temperature plots of $\Delta F^\circ/T$ varied from 10 to 30 kg.-cal./mole.

The most significant finding in this work of Marshall and Peters is that ΔH and ΔF° values are essentially the same for the four types of cellulose studied; hence, the mode of attachment of direct dyes to different cellulosic fibers is the same. To quote the authors, "This supports the view that dyeing with such dyes consists in a molecular attraction between the dye molecule and the cellulose chain molecule, the energy changes on adsorption thus being independent of the physical structure of the fiber, but highly dependent upon the molecular structure of the dye. Assuming the linking of dye and fiber to arise from hydrogen bonds, then at least two such bonds are present in the dyes tested. The differences in dyeing behavior of the various cellulosic fibers must arise solely from differences in their physical structure, particularly as it affects the effective volume of the cellulose phase for adsorbed ions." According to these authors, the fact that cuprammonium rayon will absorb more dye than viscose rayon is due to a greater number of cellulose-chain sites in the former fiber upon which dye molecules may become attached.

Recently, Fowler, Michie, and Vickerstaff [8] applied this thermodynamic treatment to equilibrium data for the dyeing of five anthraquinone-type vat dyes onto cotton at 40°C. Affinities (free energies of dyeing) ranging from -1690 to -5730 cal./mol. of dye absorbed were calculated for these dyes. The experimental data were in good agreement with theory, and indicated that the vat dyes in their leuco form at 40°C are not aggregated to any considerable extent. This is of particular interest in view of the high electrolyte concentration in vat leuco solutions. The authors concluded that the dyeing of cellulose with vat dyes proceeds in the same manner as when dyeing with direct dyes, involving the adsorption of dye anions and the division of sodium ions between fiber and solution according to the laws of membrane equilibrium. The differences in the practical dyeing behavior of vat and direct dyes appear to be due chiefly to the high electrolyte content of the vat dye bath.

Effect of Fiber Differences

Variations in type and structure of fibers have marked effects on the dyeing behavior of cellulose. This aspect of cellulosic dyeing has been fairly well investigated, but cannot be covered completely in the

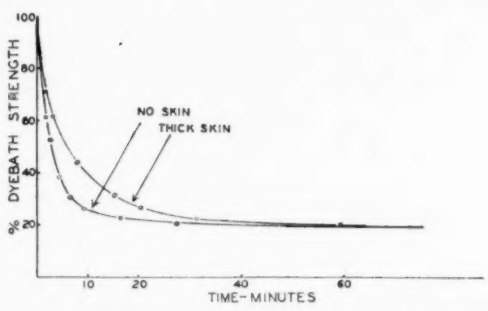


FIG. 9. *Effect of skin structure of viscose rayon on dyeing with Sky Blue FF.*

present paper. One example of fiber structure effects on dyeing will be cited.

Viscose rayon fibers differ in their physical properties and dyeing behavior, depending on certain variations in the spinning operation. For example, certain changes in the composition of the spinning bath determine the extent to which the fibers will have a skin structure. Figure 9 shows exhaustion curves for "no-skin" and "thick-skin" viscose yarns when dyed with Sky Blue FF at 90°C under identical dyeing conditions [23]. The skin structure, which is somewhat denser and somewhat more highly oriented than the core, resists the diffusion of dye, causing dyeing to be slower on the "thick-skin" fiber. Figure 10 shows cross sections of these two dyed fibers. The skin structure can be seen in the one fiber sample.

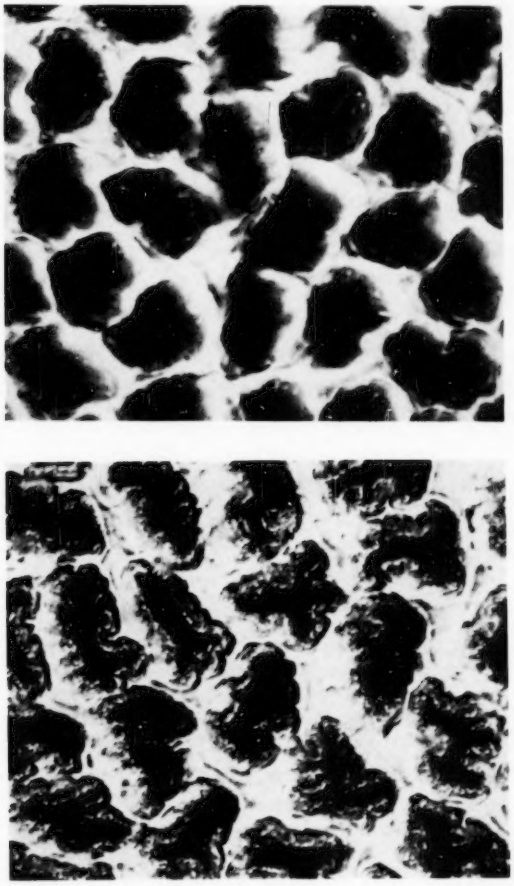


Fig. 10. *Photomicrographs of cross-sections of no-skin* (upper) *and thick-skin* (lower) *viscose fibers dyed with Sky Blue FF.*

Morehead and Sisson [14] and Hermans [10] made studies of the dyeing properties of viscose fibers with skin structure, and reported that dye can be washed out of the core more rapidly than from the skin. Elöd and Frölich [6], in more recent work, reported that viscose fibers showing the greatest difference between skin and core showed the lowest rate and extent of absorption of direct dyes. The work of Preston and coworkers [19, 20] shows that the orientation of cellulose chains in fibers causes marked differences in dyeing rates.

Other fiber variations which have an influence on dyeing include fiber size, spinning stretch, degree of polymerization, degree of swelling, and percent amorphous character.

The Dyed Fiber

Two aspects of the dyed fiber which affect reflection of light will be mentioned.

The first aspect is the effect of fiber size on the apparent color strength of a dyed skein. This is purely an optical effect, and can be seen visually by comparing two dyed rayon skeins which are of different filament size, but which contain the same amount of dye per unit weight. The fine-filament yarn will appear much lighter (weaker) than the coarse-filament yarn. It is necessary to put more dye onto the fine-fiber yarn in order to make it look like the coarser yarn. This phenomenon is known to most dyers, and is due to the greater amount of light scattered from the fine fibers. Fothergill [7] published a nomograph from which can be read the amount of additional dye necessary for correcting the appearance of the fine-fiber yarn.

The second aspect is the dichroic effect. Morton [15], from a study of this phenomenon, pictured dyed cellulose in the following manner: Dye molecules are oriented parallel to the cellulose molecular chains to which they are coordinatively bound. With respect to the fiber axis, the dye molecules therefore are oriented also, and light reflected from or transmitted by the fiber is partially polarized—that is, the dyed fiber is dichroic. The simplest experimental evidence of this effect is to look at a polarized light source through a sheet of direct-dyed Cellophane. As the dyed sheet is rotated, the change in light intensity is easily detected. Morton found that in dye crystals and elongated dye micelles, dye molecules are positioned laterally, just opposite to their orientation within a dyed fiber. This represents, perhaps,

some of the best evidence that in cellulosic dyeing, the active species is the single dye molecule; dyeing is probably not due to either the diffusion of or formation of micelles within cellulose.

Preston and Tsien [22] and Preston and Su [21], in a series of papers on the cellulose-dye complex, made a thorough study of dye orientation in fibers and its effect on reflected light. They found that fiber anistropy and the resultant dichroism of dyed fibers affect the relation between dye concentration and the intensities of reflection of polarized and unpolarized light. Fiber shape and structure also influence the reflection of light from dyed fibers. These authors showed further the relationships between dichroism, birefringence, x-ray diagrams, and fiber swelling.

Summary

The theoretical aspects of the dyeing of cellulose with substantive dyes has been reviewed.

The oriented chainlike structure of cellulose containing both amorphous and crystalline regions influences both its dyeing properties and the optical appearance of dyed fibers. Dye sorption is believed to occur only in the amorphous regions, where single molecules of dye are coordinatively bound to cellulose chains.

Dyeing appears to be a diffusion-controlled reaction which determines the rate of dye bath exhaustion. The movement of dye through a fiber is a hindered diffusion process further modified by sorption of dye.

The affinities of dyes for cellulose are obtainable from equilibrium dye absorption data, and can be expressed quantitatively in terms of ΔF° values which are of the order of 3 to 6 kg.-cal. per mole of dye sorbed. Affinities decrease with increase in temperature. Dyeing is exothermic, the values of $-\Delta H$ of the order of 10 to 30 kg.-cal./mole indicating at least two hydrogen bonds per molecule of dye.

Filament size has an effect on the appearance of dyed fibers because of differences in the light which is scattered.

The skin structure of rayons slows down the penetration of dye to the interior of the fibers.

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Relationship Between Various Parameters of a Load-Elongation Curve

Joel Lindberg*

Institute for Applied Textile Research, Gothenburg, Sweden

Abstract

This paper involves a statistical analysis of the relationship between various parameters on load-elongation curves for wool fibers in order to find low-variance single-fiber mechanical properties. No consideration is given the functional significance of these properties.

The Hookean slope and the force at 20% elongation in the wet state were found to be independent of each other for one particular sample of fiber. The area under the curve up to 20% elongation was found to be dependent upon both the Hookean slope and the force at 20% elongation, and it is therefore unnecessary to determine this area if the latter two parameters are known.

Introduction

If a wool fiber is loaded, it will extend a certain percentage of its original length. The relationship between load and elongation can be determined experimentally over a range of loads up to the breaking load and expressed graphically as a load-elongation curve. A load-elongation curve can be characterized by different parameters. Among those used are the Hookean slope, H, the load at $a\%$ elongation, F_a (a usually being 20 or 30), and the energy required to stretch the fiber $a\%$, Q_a. These parameters are shown in Figure 1, Q_a being the hatched area.

The various parameters which can be derived from such a curve have found frequent use in the correlation of fiber properties with fabric behavior. Since there is a definite relationship between chemical composition and mechanical properties [9], these parameters can also be used to detect a chemical modification of wool fibers produced by some specified treatment. The measurement of these parameters are accordingly of such importance that it might be well worth while to study the relationship between them. A method including multiple regression analysis is therefore outlined in this paper. No consideration is given here to the functional significance of the parameters.

If the load-elongation curves of two or more samples of wool fibers having different origins or having been subjected to different treatments are to be compared, the following procedure is used. From each sample a certain number of fibers are drawn at random and their load-elongation curves determined The value of the force at any point of the curve is generally assumed to be a linear function of the cross-sectional area, A, of the fiber. Within each sample the values of the cross-sectional area of different fibers are widely variant. Therefore, it is necessary to measure a large number of fibers in order to reduce the sampling variation for the mean area and, consequently, for the mean of any force value on the curve. These difficulties can be avoided by calculating parameters that are independent of the area. If the area, A, is known, the specific value p_a, force per unit cross-sectional area, can be calculated, assuming a linear relationship between F_a and A of the form $F_a = p_a \cdot A$. Another method is to measure a certain parameter on the same fiber in two different media and calculate the ratio between the two values. This

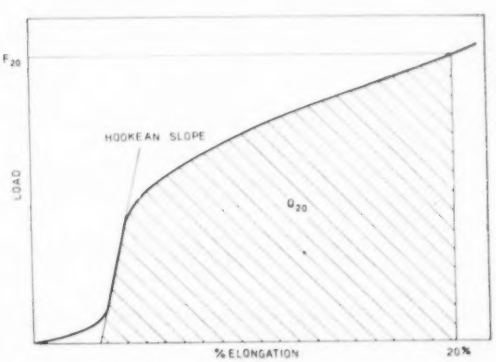


Fig. 1. *Load-elongation curve for a wool fiber.*

* Director of Research.

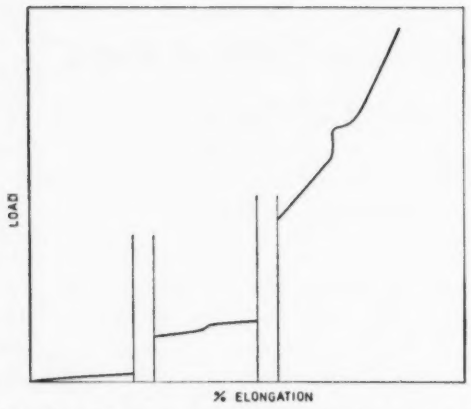


FIG. 2. *Enlargement of the uncrimping region in Figure 1, showing humps due to resonance.*

latter method has been used by Burte [1, 2] to detect slight chemical modifications of wool fibers. He measured the Hookean slope in air, H_{air}, and in water, H_{wet}, the underlying assumption being that the modification will affect only the value of H_{wet}. By taking the ratio H_{wet}/H_{air} the cross-sectional area is eliminated and a considerable reduction in the sampling variation is achieved. Burte also suggested the use of ratios such as F_a/H_{air} and Q_a/H_{air} to reduce the sampling variation in F_a and Q_a.

Experimental Conditions

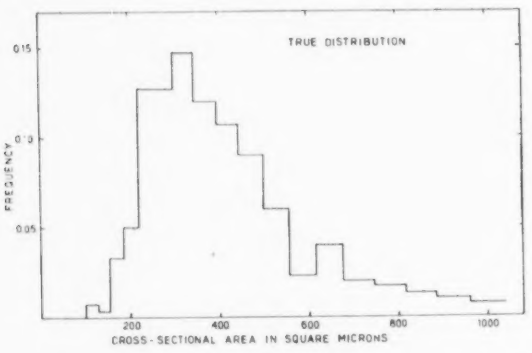
The stress-strain curves were determined with the Instron tensile tester [5]. The fibers were mounted on cellophane strips which could be attached to the load-cell and the crosshead, respectively. The length of the fiber specimen was 3.1 cm. at 0.5 g. load. The cross-sectional area, A, of the fiber was determined by means of a modified Gonsalves vibrascope [3, 4]. The value of A is calculated from the well-known string formula:

$$A = \frac{F_r}{4\rho \cdot \nu^2 \cdot l_r^2},$$

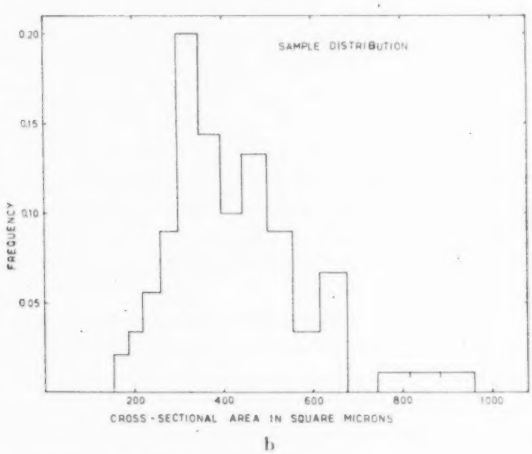
where ρ is the specific gravity, ν is the frequency, F_r is the tension, and l_r is the length of the fiber at resonance.

The cellophane strip at the lower end of the fiber was attached to the needle of a gramophone pickup, and the pickup was fastened to the crosshead. The deflection of the needle in the fiber direction was negligible. The pickup was fed by an oscillator with an A.C. voltage of 1,200 cycles/sec., the vibration of the needle being transversal to the fiber axis. When the load, which increases continuously with elongation, reached the value corresponding to the resonance frequency, a bump was produced in the curve, as can be seen from Figure 2. This method has also been used at Textile Research Institute [7]. The load at this point is F_r. The length l_r of the specimen at this point may be calculated from the length at 0.5 g. load. The rate of elongation used was 1 cm./min. The fiber was first stretched 2%–3% in air at 65% R.H. to produce the Hookean slope at these conditions. After relaxation for 5 min. in water, the whole curve in water up to the breaking point was determined. Further details about the experimental conditions have been published elsewhere [6]. From the curves the following parameters were calculated: H_{air}, H_{wet}, F_{20}, and Q_{20}.

Originally the experimental material consisted of



a



b

FIG. 3. *Frequency distribution of fineness.*

nine samples with ten fibers in each sample. All nine samples were taken from the same lot of wool top, but were subjected to different treatments before the measurements. It was found, however, that all samples could be regarded as drawn from the same population of fibers; therefore, all ninety fibers are treated as one sample in the statistical analysis.

Statistical Analysis of Data

When the sampling of fibers for the experiment was made, the operator tried to pick out fibers at random. It is important to know if this sampling really is unbiased or if it is influenced in some way by the operator. Therefore, the distribution of cross-sectional area in the experimental sample was compared with the distribution of cross-sectional area in the lot measured by a different method. The latter method was a microscopical determination of fineness according to standard methods [10], and was assumed to give a good estimate of the true distribution. In Figure 3 the frequency curves for the distributions obtained by the two methods are shown. It is seen that the sampling by the operator was somewhat biased. Moreover, both curves show a very marked skewness. Because of this skewness, some values fall far away from the mean, as can be seen from Figure 4, where F_{20} is plotted against A. If the regression of F_{20} upon A is determined, these extreme values will influence the value of the regression coefficient to a great extent. In order to eliminate this influence, the values of A were transformed to make the distribution more symmetrical. In Figure 5 the distribution $\sqrt{A}$ is shown. This transformation is considered to be sufficient. Since all measured parameters show approximately the same skewness as A, they were transformed in the same manner. In Figures 6, 7, and 8 examples of the relationship between different parameters are given. In all cases it was found that the relationship between different parameters was linear. One condition for the regression analysis is that the variance of the dependent variable is constant for different values of the independent variable. From the graphs it can be seen that this condition is satisfactorily fulfilled.

If the distributions of the variables had been representative for their populations, the data could have been treated as a two-dimensional population. Since this is not the case, the difficulties can be avoided by regarding the values of one variable as being constant selected values. The relationship between different parameters of the load-elongation curve was calculated by means of multiple regression analysis. In general, the correlation method given by Snedecor was used [8]. All details of the calculations are omitted here, but the original data are given in Table I. If a dependent variable is related linearly to two independent variables, this relationship could be given by an equation of the form

$$y = b_{y1\cdot 2}x_1 + b_{y2\cdot 1}x_2 + a,$$

where y is the dependent variable, x_1 and x_2 are the independent variables, a is a constant, and $b_{y1\cdot 2}$ and $b_{y2\cdot 1}$ are the partial regression coefficients. The coefficient $b_{y1\cdot 2}$, for instance, gives the regression of y on x_1 independent of x_2. The values of $b_{y1\cdot 2}$ and $b_{y2.1}$ could be calculated by the method of least squares, and the significance tested against their respective standard errors by means of the t-test.

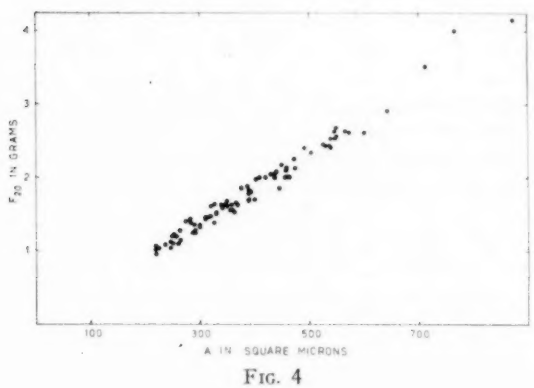


FIG. 4

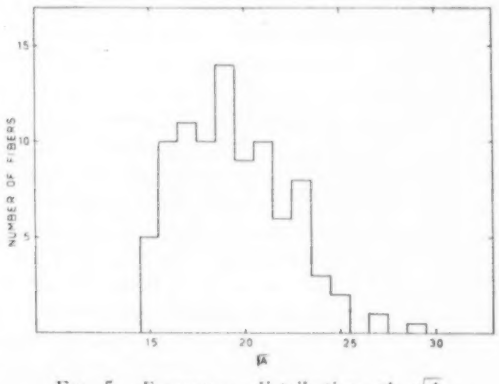


FIG. 5. *Frequency distribution of* $\sqrt{A}$.

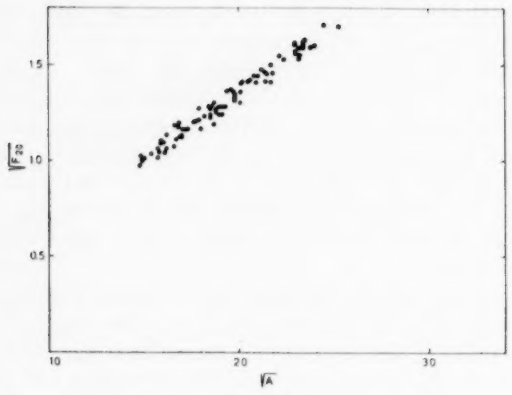


FIG. 6

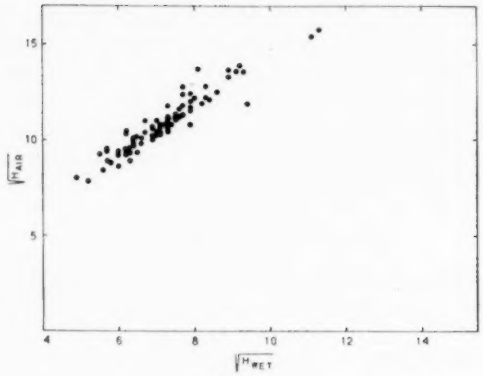


FIG. 7

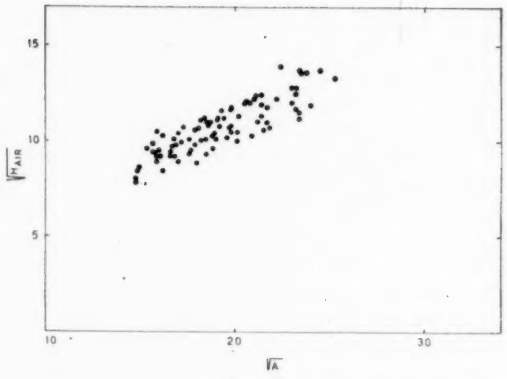


FIG. 8

Instead of the partial regression coefficient $b_{y1\cdot2}$, the standard partial regression coefficient $b'_{y1\cdot2}$ could be calculated, which is somewhat simpler. The relation between these two coefficients is given by

$$b_{y1\cdot2} = b'_{y1\cdot2} \cdot \frac{s_y}{s_1},$$

where s_y and s_1 are the standard deviations of y and x_1, respectively, expressed in appropriate units. The standard errors of $b'_{y1\cdot2}$ and $b'_{y2\cdot1}$ have the same value,

$$s_{b'} = \sqrt{\frac{1 - R^2}{(1 - r_{12}^2)(n - 3)}},$$

where R is the multiple correlation coefficient, r_{12} is the correlation coefficient for x_1 and x_2, and n is the number of fibers. Only the values for $b'_{y1.2}$ and $b'_{y2.1}$ will be given here, other values being of no direct interest.

In order to obtain an estimate of how close the data fit to the equation above, the relative error variance can be calculated. The part of the total variance given in relative units (total variance = 1) which is explained by the regression is equal to R^2 or r^2. That part which is unexplained by the regression is the error variance, and the relative error variance is therefore equal to $(1 - R^2)$ or $(1 - r^2)$.

As mentioned before, it has been suggested by Burte that parameters such as H_{wet} and also F_{20} and Q_{20} should be compared with H_{air} in order to eliminate the influence of A, thereby saving the trouble to make an independent measurement of A. By the technique used in the present experiments it is just as easy to measure A as H_{air}, and therefore it might be interesting to see which of these two parameters gives the lowest residual variance when used together with H_{wet} or F_{20}.

In the equations given above, $\sqrt{H_{wet}}$ is substituted for y, $\sqrt{A}$ for x_1, and $\sqrt{H_{air}}$ for x_2. The values for $b'\sqrt{H_{wet}}\sqrt{A}\cdot\sqrt{H_{air}}$ and $b'\sqrt{H_{wet}}\sqrt{H_{air}}\cdot\sqrt{A}$ obtained from the calculations are 0.167 and 0.799, respectively. The standard error, s_f, is 0.0730. This gives t-values of 2.28 and 10.9, respectively ($t_{0.05} = 1.99$ for 84 degrees of freedom). These results indicate that if the Hookean slope is measured in water for different fibers having the same cross-sectional area, there is a strong positive correlation between this slope and the slope measured in air. This is in complete accord with the results given by Burte [1]. On the other hand, if fibers having the same value of H_{air} have their Hookean slopes measured in water, these latter values are also slightly correlated with cross-sectional area. This could be concluded from a comparison of the t-values with $t_{0.05} = 1.99$.

TABLE I. VALUES OF THE DIFFERENT PARAMETERS USED IN THE STATISTICAL CALCULATIONS

$\sqrt{A}$ (μ^2)	$\sqrt{H_{air}}$ (g.)	$\sqrt{H_{wet}}$ (g.)	$\sqrt{F_{20}}$ (g.)	$\sqrt{Q_{20}}$ (relative)	$\sqrt{A}$ (μ^2)	$\sqrt{H_{air}}$ (g.)	$\sqrt{H_{wet}}$ (g.)	$\sqrt{F_{20}}$ (g.)	$\sqrt{Q_{20}}$ (relative)
20.1	10.5	7.3	1.30	89	18.6	10.8	7.2	1.28	87
19.8	11.8	7.7	1.31	93	20.8	12.0	7.9	1.44	101
18.2	11.1	7.3	1.23	87	21.0	12.2	8.3	1.44	101
18.4	11.2	7.5	1.28	90	20.6	12.1	8.4	1.42	94
20.5	12.0	7.9	1.41	97	23.2	12.5	8.6	1.55	110
21.4	11.3	7.5	1.46	100	18.8	10.3	7.1	1.27	86
15.9	9.2	6.0	1.09	75	19.6	10.2	6.5	1.37	94
23.2	11.7	7.9	1.59	112	17.0	10.4	7.1	1.16	81
21.5	10.6	6.9	1.45	97	16.6	9.2	6.2	1.18	79
17.2	9.9	6.5	1.16	82	21.8	10.7	6.9	1.46	99
16.7	9.7	6.4	1.11	73	23.4	13.7	8.1	1.60	111
18.8	9.6	6.3	1.25	88	16.2	8.4	5.6	1.06	73
23.4	11.2	7.5	1.59	110	17.3	10.8	7.1	1.16	81
18.7	11.0	7.5	1.30	92	16.1	9.2	5.5	1.04	69
20.2	11.3	7.7	1.41	99	23.5	13.6	9.1	1.63	114
16.2	10.3	6.2	1.13	77	19.7	10.7	7.1	1.36	87
21.4	12.4	7.9	1.41	99	21.7	11.0	7.3	1.50	99
19.8	11.7	7.9	1.33	95	16.0	9.5	6.2	1.09	77
18.5	11.0	7.3	1.24	84	26.7	15.4	11.1	1.87	137
22.2	12.2	8.0	1.55	109	24.5	13.7	8.9	1.61	109
15.0	8.6	6.0	1.01	71	16.8	10.1	6.9	1.19	85
18.2	10.0	6.9	1.23	86	29.3	15.8	11.3	2.03	142
20.9	10.3	7.0	1.41	99	15.9	10.5	6.2	1.10	78
19.0	10.1	6.4	1.24	85	19.1	11.2	7.3	1.24	86
23.8	13.6	9.3	1.59	111	15.8	9.4	6.0	1.04	73
15.9	8.9	6.3	1.09	78	16.6	9.4	6.5	1.07	71
19.3	11.6	7.6	1.28	89	19.2	10.8	7.4	1.28	91
17.0	10.4	7.0	1.12	79	15.7	9.9	6.4	1.06	75
16.8	9.2	6.2	1.17	82	20.1	10.0	6.9	1.40	95
17.9	10.6	7.3	1.21	87	18.7	11.0	6.7	1.19	81
24.0	11.9	9.4	1.60	115	23.4	11.5	7.9	1.62	117
14.9	8.4	5.6	1.00	70	17.9	9.8	6.6	1.27	88
14.8	8.0	4.9	.97	65	15.4	9.6	6.3	1.03	71
15.7	9.4	5.7	1.01	71	14.8	7.8	5.2	1.02	70
21.1	12.4	7.7	1.36	94	19.8	10.5	7.3	1.34	93
18.9	10.4	6.7	1.28	89	19.4	11.2	7.6	1.36	94
18.5	10.1	6.9	1.22	87	18.1	10.7	7.9	1.28	91
25.3	13.3	8.9	1.70	117	23.0	12.8	8.3	1.57	105
17.7	9.5	5.7	1.20	81	21.7	11.8	7.3	1.41	98
18.5	9.3	6.2	1.27	89	21.2	11.0	7.0	1.48	101
21.4	11.9	8.2	1.41	98	17.6	9.3	6.3	1.20	83
23.0	12.0	7.9	1.56	105	23.2	12.8	7.7	1.53	105
18.0	8.8	5.8	1.17	79	19.8	10.8	7.3	1.33	94
17.6	10.1	6.6	1.20	81	16.9	9.8	6.6	1.12	79
22.4	13.9	9.2	1.53	108	17.0	8.9	5.7	1.13	79

If cross-sectional area alone is used to eliminate the variation in Hookean slope in water, the relative error variance is 22.7%; and if the Hookean slope measured in air is used for the same purpose, the relative error variance is 9.98%.

The lowest error variance is thus obtained with the use of the Hookean slope measured in air. This variance can be reduced further to 9.37% by introducing cross-sectional area as a second independent variable, as has been done in the multiple regression analysis above. If both values of b' are significant, it follows that this reduction in error variance is also significant. The size of the reduction, however, is so small that it is doubtful if there is any practical use in carrying out the multiple regression analysis. It is concluded that even if the cross-sectional area is known, it is better to use the Hookean slope measured in air to reduce the error variance in Hookean slope measured in water.

Exactly the same calculation was carried out with $\sqrt{F_{20}}$ as the dependent variable instead of

$\sqrt{H_{wet}}$. In this case:

$$b'\sqrt{F_{20}}\sqrt{A}\cdot\sqrt{H_{air}} = 0.971;$$
$$b'\sqrt{F_{20}}\sqrt{H_{air}}\cdot\sqrt{A} = 0.0182.$$

The standard error is 0.0376. The t-values are 25.82 and 0.484, respectively ($t_{0.05} = 1.99$). The value of $t = 0.484$ is, of course, not significant, and hence there is no correlation between the force at 20% elongation and the Hookean slope in air when the cross-sectional area is kept constant. The relative error variance is 2.53% when $\sqrt{F_{20}}$ is plotted against $\sqrt{A}$, and 22.2% when $\sqrt{F_{20}}$ is plotted against $\sqrt{H_{air}}$. The cross-sectional area is thus far more effective in reducing the error variance in F_{20} than is the Hookean slope measured in air. This result is the opposite to that obtained with H_{wet}, and shows that the technique used by Burte cannot readily be extended to other parameters than H_{wet}.

Supposing that the Hookean slope in air has not been measured. What, then, is the relationship between the Hookean slope in water and the force at 20% elongation when the cross-sectional area is kept constant?

If $\sqrt{H_{wet}}$ is substituted for $\sqrt{H_{air}}$, the following results are obtained:

$$b'\sqrt{F_{20}}\sqrt{A}\cdot\sqrt{H_{wet}} = 0.923;$$
$$b'\sqrt{F_{20}}\sqrt{H_{air}}\cdot\sqrt{A} = 0.0739.$$

The standard error is 0.0356, and the t-values are 25.9 and 2.08, respectively.

It is seen from the t-values that there is a slight positive correlation between the Hookean slope and the force at 20% elongation. For practical purposes, however, these two parameters can be regarded as independent, and each of them might furnish valuable information on the behavior of the wool fiber.

It has been suggested that the work necessary to stretch the fiber some percentage should be used to characterize the curve. It might, however, be expected from the form of the curve that Q_{20}, for instance, is dependent upon both H_{wet} and F_{20}. A multiple regression analysis with $\sqrt{Q_{20}}$ as the dependent and $\sqrt{H_{wet}}$ and $\sqrt{F_{20}}$ as the independent variables gave the following results:

$$b'\sqrt{Q_{20}}\sqrt{F_{20}}\cdot\sqrt{H_{wet}} = 0.868;$$
$$b'\sqrt{Q_{20}}\sqrt{H_{wet}}\cdot\sqrt{F_{20}} = 0.136.$$

The standard error is 0.0321. The t-values are 27.0 and 4.24, respectively ($t_{0.05} = 1.99$).

Both regression coefficients are significant, which means that the work necessary to stretch the fiber 20% can be regarded as being linearly related to the Hookean slope and the force at 20% elongation. The relative error variance is reduced to 1.88%, which is not more than can be ascribed to experimental error. If the variance of $\sqrt{Q_{20}}$ is reduced by means of $\sqrt{A}$, the error variance is as high as 5.18%. The area under the curve, Q_{20}, is therefore not an independent parameter on the load-elongation curve.

Conclusions

It is, in general, very time-consuming to evaluate mechanical properties of wool fibers by individual measurements. It is therefore necessary to make use of every possibility to reduce the amount of work. This can be done partly by reducing the number of fibers to be measured and partly by concentrating on a few of the independent properties. Low-variance properties must be selected in order to reduce the number of fibers necessary to measure. It has been shown that if the Hookean slope is measured in water, it is better to reduce the variance by using the Hookean slope measured in air than by using the cross-sectional area, even if the cross-sectional area happens to be known. For the force at 20% elongation, the reverse is true. In this case, the greatest reduction in error variance is obtained by using cross-sectional area.

The area under the curve up to 20% elongation, which is the same as the work necessary to stretch the fiber 20%, is a function of both the force at 20% and the Hookean slope. This area is therefore not an independent parameter, and measurement of this area gives no information which cannot be obtained by knowledge of the Hookean slope and the force at 20% elongation.

Acknowledgment

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Properties of Apparel Wools
IV. Physical Properties of Single Fibers*

T. F. Evans and D. J. Montgomery

Textile Research Institute, Princeton, New Jersey

Abstract

A detailed report is presented on the physical properties of single wool fibers withdrawn from four master samples at various stages of worsted processing. The experimental procedure for sampling and testing is described. The following properties were taken from the force-extension curve: slope in the Hookean region, force at 20% extension, energy for 20% extension, force at break, and extension at break. A study of the correlation of these properties with cross-sectional area was made, and it was observed that at a given station in processing there is no important difference between wools of different origin when forces are reduced to stresses by division by the area. The changes in the force-extension properties during processing were found to be definite, but not great. Aging subsequent to certain operations was found to have negligible effect on physical properties except at very low extensions, where crimp recovery with aging occurs in single fibers free from constraints.

Introduction

As part of the Wool Research Project carried out at Textile Research Institute and the Forstmann Woolen Company, a study was made of some physical parameters from the force-extension curves for single wool fibers. The results of this study were summarized by von Bergen and Wakelin in the first paper [8] of this series. In the present paper these results are considered in detail.

The first purpose of the single-fiber study was to determine what changes take place in the fibers during the several steps of worsted manufacture, and during the aging periods following certain operations in manufacture. The second purpose of the study was to determine what differences in fiber properties exist between fine and medium wools, and between wools of domestic and foreign origin. Accordingly, samples of the four master wools described in the first paper of this series were selected at various stages in processing, and force-extension curves were run on single fibers withdrawn from the samples. The resulting data were analyzed to permit conclusions to be drawn about changes during processing and about differences between wools.

* Parts I, II, and III appeared in the February, 1952, July, 1952, and July, 1953, issues of TEXTILE RESEARCH JOURNAL, respectively.

This article is a report of work conducted as part of the Wool Research Project sponsored by the American Wool Council, the International Wool Secretariat, the National Wool Trade Association, the United States Department of Agriculture (RMA Contract A-1s-30934 supervised by the Western Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration), the Office of Naval Research, and by a number of American wool manufacturers.

Part I: Experimental Procedure

Materials

The four master wools of the Wool Research Project described by von Bergen and Wakelin [8] were used in this study. These consisted of two fine wools—a 70's grade Merino of Australian origin and a 64's grade Rambouillet from the U. S. Sheep Experiment Station at Dubois, Idaho—and two medium wools—a 58's grade Targhee from the Dubois Experiment Station and a 58's grade Corriedale from New Zealand. Fibers were selected from each of these master wools for physical tests at the following stages of processing: grease wool, scoured wool, top, roving, unsteamed singles yarn,* steamed doubles yarn,† grey cloth, ready-to-dye cloth, and finished cloth. In order to study the aging process in top, roving, and yarn, groups of fibers from each of these four stages were tested at several intervals of time.

To the extent that physical properties vary with fiber length, the method of selection of fibers needs consideration. Since an average based on fibers chosen by a random process will reflect the known changes in staple length through the various stages of processing, a deliberately nonrandom selection of fibers was made. At all processing stages an attempt was made to select fibers of approximately the raw staple length for each of the four wools, in order to reduce to a minimum the effect of short fibers which would be combed out. Furthermore, the variability between fibers is probably smaller, and therefore the sensitivity of the comparisons in which we are interested is greater than would be the case with a random sample. The data are not quite so general in application, however, because nothing has been learned about the physical properties of the unusually long or short fibers.

At each of the processing stages studied, fibers were selected systematically so as to obtain information on the homogeneity of the samples. For instance, in the grease state several staples were selected from those entering the scouring train at a number of times, and several fibers were tested from each staple. At later stages in the processing, sets of fibers were chosen in analogous fashion from specific gills, spindles, and so on.

* U. S. fine wool not sampled.
† Australian fine wool not sampled.

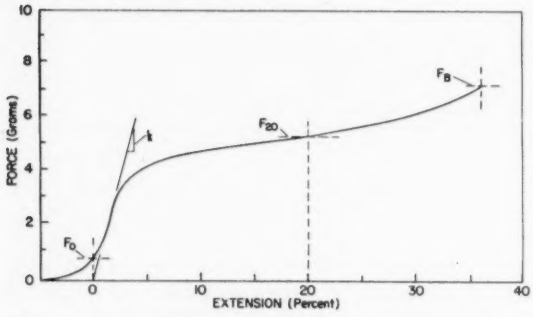

FIG. 1. *Typical force-extension curve to break for single wool fiber.*

Testing Procedure

For the aging studies with top, roving, and yarn, two types of force-extension tests were made. The first test, here designated *T-1*, is a destructive test in which each fiber is extended to break at a constant rate of extension. Figure 1 shows a typical force-extension record for this test. This test was made on sets of fibers at each stage of processing in order to study the effect of processing, and also on sets of fibers withdrawn from the above-mentioned assemblies at different times after processing in order to study the effects of aging. A new set of fibers is, of course, required for every test. Test *T-1* permits determination of parameters involving all parts of the force-extension curve. The second test, designated *T-2*, is a nondestructive test in which individual fibers are extended through the Hookean region only (that is, just past the knee in Figure 1), and then returned to the unstretched condition for subsequent tests. Test *T-2* was conducted on sets of fibers withdrawn from assemblies in which aging is suspected to be important. The same set of fibers was used throughout the entire aging period. This test permits determination of parameters in the low-extension region of the force-extension curve; it is run at a higher sensitivity than test *T-1* so as to enlarge this low-extension region.

The testing consisted of three parts: mounting the fiber, determining its cross-sectional area, and getting the force-extension record. During the course of the investigation, the techniques progressed through a series of evolutionary forms, and only the procedure adopted for the bulk of the tests will be described.

Fibers were mounted between $\frac{1}{2}$ in. $\times$ $\frac{1}{4}$ in. tabs with Duco cement for ease of handling. For tests at 65% R.H., one of these tabs for each fiber was of brass 0.005 in. thick, and the other was of cellulose acetate 0.015 in. thick. The brass tabs were found

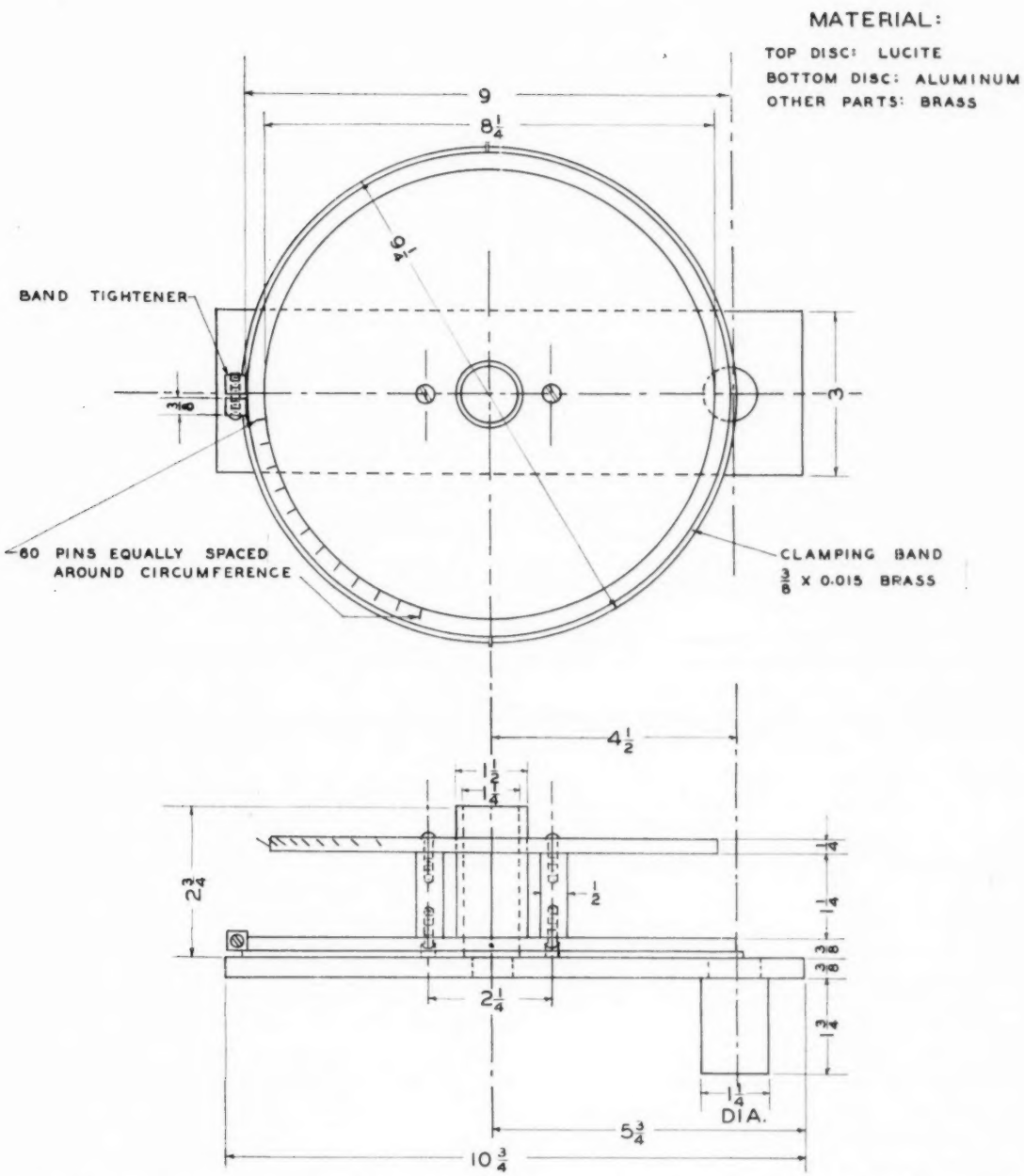

FIG. 2. *Circular jig for testing and storing single fibers. In use the jig rests on an anvil as shown, which is carried in the crosshead of the tensile testing machine. The jig is revolved until the bottom tab of the fiber under test is exactly under the strain-sensing element of the tensile tester. At the conclusion of a test the jig may be removed for storing the fibers.*

convenient in the subsequent cross-sectional area determination, which requires the fiber to be put under a known tension. The brass tabs could be cut to a known weight and used repeatedly, obviating the necessity of weighing them each time, and several sets were prepared. These tabs were found to be unsuitable for tests in water because the cement would not hold, and for these experiments both tabs were of cellulose acetate. A segment of fiber approximately 1 in. long was included between the tabs.

Jigs of the type shown in Figure 2 were constructed so that groups of fibers could be tested easily and with a minimum of handling. After a fiber was mounted and placed on a jig, it could be moved about readily without disturbance. This reduction in fiber handling was particularly necessary in test *T-2*, in which each fiber was tested several times over a period of a year.

Average cross-sectional areas for the 1-in. fiber segments were determined by the vibroscope method, which has been described by Montgomery and Milloway [4], among others. In this method a known length of fiber under tension is subjected to a transverse audio-frequency vibration, and the frequencies at resonance are observed. For most of the measurements reported here, the audio-frequency driving force was transmitted to the fiber electrostatically. The first overtone (that is, the frequency of the second mode) of the vibrating fiber was used to estimate the area by the equation

$$A = 10^8 T/4\rho L^2(f_2/2)^2,$$

where A = average cross-sectional area (μ^2), T = tension (dynes), L = fiber length (cm.), f_2 = first overtone (c.p.s.), and ρ = density = 1.305 g./cm.^{3} for wool.

No correction was made for fiber stiffness, and the cross-sectional areas as reported here are therefore about 2%–4% low, the greatest error occurring with the medium wools. Most measurements were made under a fiber tension of approximately 150 mg. The bias in the area determination implies a corresponding error of the same amount, but of opposite sign, in those physical properties that were reduced to unit cross section.

The length of the fiber was measured to the nearest hundredth of a centimeter under the applied tension. In some cases of unusual crimp, the fibers were not quite fully straightened by the applied weight, and the error in cross-sectional area will be somewhat less for these.

With a given fiber the measurement of the fundamental frequency or of the first overtone could be repeated within 1% or 2%, but the overtone was frequently different from twice the fundamental, presumably owing to nonuniformity of the cross-sectional area along the length of the fiber. Differences up to 5% in frequency occur in practice, and these can probably be accounted for by nonuniformity, as discussed by Montgomery [3].

Following the area determination, the fibers were extended on an Instron Tensile Tester at 70°F. in air at 65% R.H., or in water. In test *T-1* the fibers were extended to break at a rate of 0.5 in./min. and at a sensitivity of 10 g. full scale. A continuous record of the force against extension was obtained on the recorder of the Tensile Tester, and at the same time the energy absorption of each fiber was recorded continuously by an electronic or a mechanical integrator incorporated into the recorder assembly, as described by Montgomery [2].

In view of the large number of fibers (over 5,000) which were studied in test *T-1*, I.B.M. punched-card equipment was used for many of the routine calculations, such as the determination of cross-sectional area from the vibroscope data, and the initial summations for statistical evaluation. All these calculations were made on a 602A calculating punch. Auxiliary equipment included a card punch, sorter, tabulator, reproduced, and collator. Besides reducing very greatly the time required for routine calculations, the punched-card machines facilitated the development of distributions of the various parameters studied. This development is not reported here, in view of its limited applicability resulting from the biased selection of fibers.

For test *T-2* the fibers were extended to the knee of the force-extension curve (see Figure 1) at a rate of 0.1 in./min. and at a sensitivity of 5 g. full scale; the fibers were then contracted at the same rate until the force on the fiber returned to zero. Following the test, the fiber was allowed to stand in a relaxed position on a jig until time for a subsequent test.

Part II: Results of Tests

Correlation of Parameters with Cross-Sectional Area

From the force-extension curve to break, a typical example of which is shown in Figure 1, certain parameters must be chosen to reduce the amount of data to manageable proportions. The following list

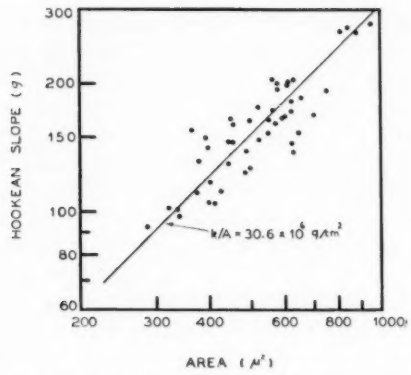

FIG. 3. *Scatter diagram for Hookean slope,* k, *against cross-sectional area,* A, *for a group of fibers withdrawn from U. S. medium wool top.*

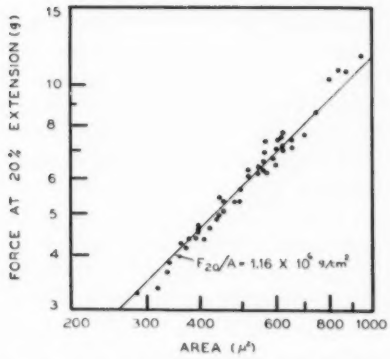

FIG. 4. *Scatter diagram for force at 20% extension,* F_{20}, *against cross-sectional area,* A, *for a group of fibers withdrawn from U. S. medium wool top.*

gives the parameters chosen to describe the force-extension curve. The ranges given are for a typical group of fibers selected from a 58's top; an estimate of the range likely to be found for the area has been included.

Property	Range
Hookean slope (k)	80–240 g.
Force at 20% extension (F_{20})	3–10 g.
Energy for 20% extension (E_{20})	0.5–1.6 g.-cm./cm.
Force at break (F_B)	3–14 g.
Extension at break (e_B)	9%–47%
Cross-sectional area (A)	300–900 μ^2

It might be expected that part of the variability in the physical properties is a reflection of the variation in cross-sectional area of the fiber, at least for the properties concerned with force. This expectation is indeed fulfilled, as can be seen from Figures 3 and 4, where the Hookean slope, k, and the force at 20% extension, F_{20}, respectively, are plotted against the area, A, for a group of fibers from a medium wool top. On these logarithmic plots 45° lines represent a constant k/A and F_{20}/A. The experimental values lie close about such lines, and hence it is seen that the physical properties of the fibers in this sample are approximately constant on a unit-area basis.

Throughout this study the scatter in the Hookean slope was found to be greater than the scatter in the force at 20% extension. This behavior seems to be associated at least partially with the crimpiness in the fibers. As an empirical measure of the degree of crimp there has been selected F_0, the force at zero extension, defined as the force at the intersection of the prolonged Hookean slope line with the extension axis (*cf.* Figures 1 or 9). The association is indicated in Figure 5, in which the modulus k/A is plotted against the stress at zero extension, F_0/A. A more thorough study of the relationship between the crimp and the measured elastic modulus in other types of wool samples has been reported elsewhere by Evans [1].

The relative variability of the stress at different extensions was studied with the group of medium wool fibers considered in Figures 3–5. Out of 48 fibers, the 26 which reached an extension of at least 36% before breaking were selected. For these fibers Figure 6 shows the average stress and the standard deviation of the stress at successive points along the force-extension curve.

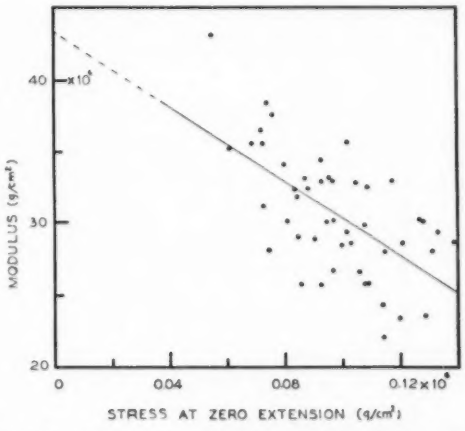

FIG. 5. *Scatter diagram for modulus* k/A *against stress at zero extension,* F_0/A, *for a group of fibers withdrawn from U. S. medium wool top.*

The breaking force of a fiber depends on the cross-sectional area, but is more variable on a unit-area basis than are other force measurements. Figure 7 shows the breaking properties for the fibers considered in Figures 3–5. The curve drawn is the average curve from Figure 6. The breaking points, both above and below 36% extension, follow the average curve very well. This finding suggests that no great amount of necking occurs at the break, since otherwise the breaking points would tend to lie somewhat to the right of the average curve.

Aging Studies

The effects of aging at the top, roving, and yarn stages were studied by both tests *T-1* and *T-2*. Whereas those parameters derived from the high-extension region of the force-extension curve can of course be obtained only by test *T-1*, certain parameters may be evaluated by both single-fiber tests. Apart from changes in precision resulting from different sensitivities and changes depending on different rates of extension, there are changes in the precision of estimates of these parameters arising from statistical considerations. For example, with regard to measurements of the Hookean slope (and the derived quantity, elastic modulus = Hookean slope/cross-sectional area), both tests are capable of furnishing estimates of mean values for the wool lots at principal stations in processing and throughout the aging periods. But test *T-1*, because it takes a larger number of fibers at each stage, is capable of giving a more precise estimate of the mean at a given *station* and hence gives better estimates of mean property values through processing. Test *T-2*, on the other hand, because it deals with the same fibers throughout aging, is capable of giving a more precise estimate of the effects of *aging*. Estimates of the same parameter by the two tests (when possible) were found to be consistent, and hence it appears that no serious difference is introduced by the difference in testing procedures.

With respect to the *T-1* test, the effect of aging on wool may be simply stated: no evidence exists to indicate a significant change with aging time in any of the parameters characterizing the medium- or high-extension region of the force-extension curve. For example, Figure 8 shows the mean elastic modulus, stress at 20% extension, and breaking stress for fibers from the top stage for the four master wools as a function of time after processing. Each point is an average derived from 48 fibers. Fibers from roving and yarn give similar results; no consistent trend with aging time is evident.

With respect to the *T-2* test, however, the decrease in variability by using the same fibers at different times and the increase in precision by using a higher force sensitivity and slower extension rate make it possible to establish certain trends in parameters of the low-extension region. In Figure 9 the *uncrimping region* is taken to be the portion of the curve from the beginning of the extension to the beginning of the Hookean region. Visual examination of the fiber during extension shows that the crimp is pretty well removed at the end of this portion of the extension. The task is now to select certain parameters to characterize the behavior during uncrimping. One natural

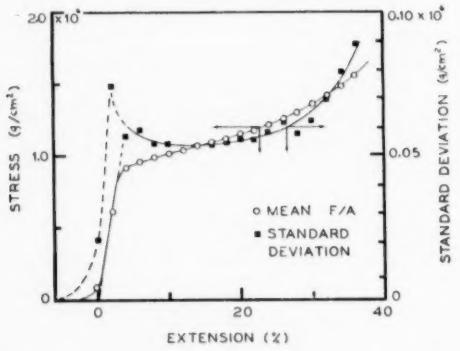

FIG. 6. *Average stress against extension for a group of fibers withdrawn from U. S. medium wool top. The squares show the standard deviation of the stress at points along the stress-strain curve.*

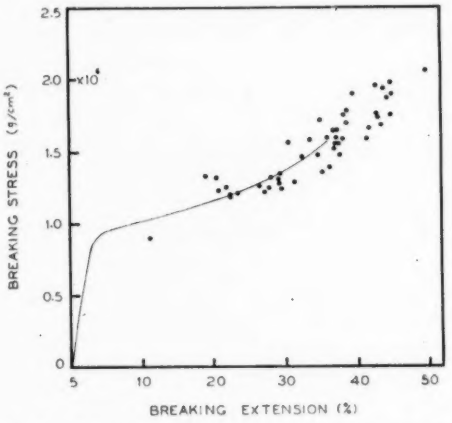

FIG. 7. *Scatter diagram for breaking stress, F_B/A, against extension at break, e_B, for a group of fibers withdrawn from U. S. medium wool top.*

choice is the uncrimping energy, E, assumed to be proportional to the stippled area in Figure 9. This property has the following advantages: it possesses a fairly direct physical interpretation; it is unambiguously defined; and it represents the entire uncrimping portion of the curve. It has the disadvantage of being laboriously determined, even when approximation methods are used.

To obtain a parameter which gives information about the *force* necessary to pull a fiber to an uncrimped state, there was selected the quantity F_o, defined earlier as the value of the force at the point of intersection of the prolonged Hookean slope line with the horizontal axis. The parameter F_o has these advantages: it is related to the stiffness of the fiber crimp; it is unambiguously determined; and it can be quickly and easily measured. It has the disadvantages of being incapable of direct physical interpretation and of being an arbitrary index.

To obtain a parameter which gives information about the *contraction* resulting from the existence of crimp in a fiber, the distance x was arbitrarily selected; this distance is the difference between the abscissa corresponding to the ordinate 0.20 F_o on the force-extension curve and the abscissa at the intersection of the prolonged Hookean slope line with the horizontal axis. This distance, of course, is smaller than the actual contraction due to crimp, which is presumably the abscissa from the beginning of the curve to the intersection of the extended Hookean line with the horizontal axis. But this point is not easily determined because of the high order of contact between the curve and horizontal axis. The parameter x has these advantages: it is related to contraction due to crimp; it is unambiguously determined; and it can be easily measured. It has the disadvantages of not having direct physical interpretation and of being an arbitrary index.

It might be hoped that the product of the two easily measured quantities, F_o and x, could be used as a convenient substitute for the laboriously measured E. This hope seems to be justified, as will be shown later, and the product $F_o x$ has the advantages of being related directly to energy to uncrimp, of being unambiguously determined, and of being easily measured and calculated. It has the disadvantages of not having direct physical interpretation and of possessing considerable arbitrariness.

The results presented in this section have been obtained chiefly in a study of two sets of single fibers withdrawn from New Zealand medium wool assemblies. The first set, containing 45 fibers, was taken from top; the second set, also containing 45 fibers, was taken from unsteamed yarn. Figure 10 is a logarithmic plot of crimp stiffness, F_o, against cross-sectional area, A, for the individual fibers of the two sets

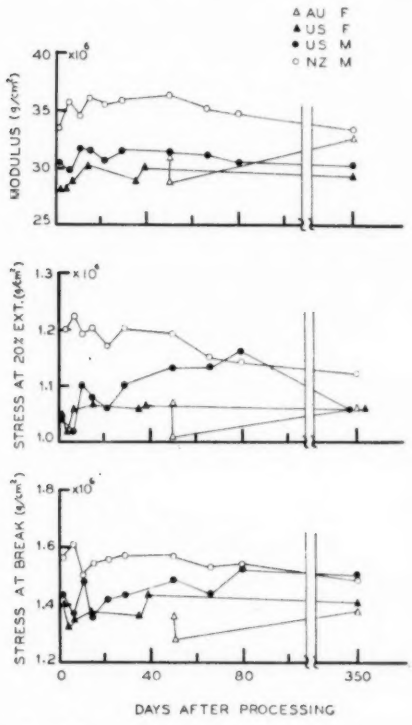

FIG. 8. *Effect of aging on stress-strain properties for single fibers withdrawn from top, and aged free from constraints.*

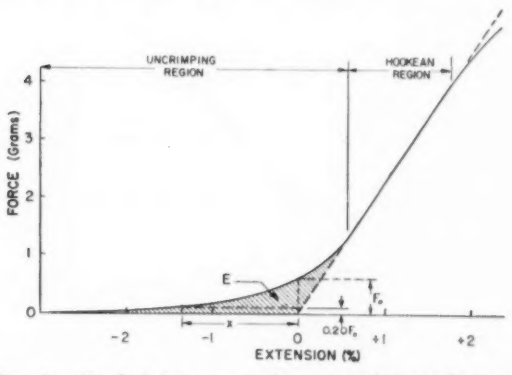

FIG. 9. *Typical force-extension curve for single wool fiber in the low-extension region.*

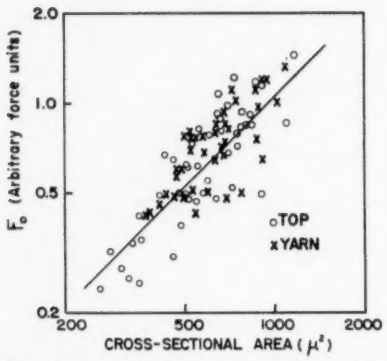

FIG. 10. *Scatter diagram for crimp stiffness,* F_o, *against fiber cross-sectional area,* A, *for single New Zealand medium wool fibers.*

at a specified time after their withdrawal from the assembly. A fairly strong correlation is evidenced by the clustering of the points about a line. The line drawn is of unit slope, corresponding to a law of direct proportionality between F_o and A. Actually, a better fit is obtained with a somewhat steeper line, but we do not wish to consider this refinement in the present paper. Figure 11 shows a logarithmic plot of the product $F_o x$ against E for the individual fibers of the two sets. The points lie very close about a 45° line, and this clustering is strong evidence for a law of proportionality between $F_o x$ and E. As a consequence of this high degree of correlation, it has been considered valid to study the product $F_o x$ as a substitute for E.

No significant difference in level between top and yarn (unsteamed) was observed with any of the three parameters studied (F_o, x, $F_o x$). However, there was observed a difference in behavior upon aging of single fibers free from the constraints in the assembly. Figure 12 shows the aging behavior of F_o/A, the crimp stiffness divided by the area of the fiber. The values plotted are arithmetic means for the 45 fibers in each set, normalized to their value at long aging times. It is seen that the fibers from top start out at a value only about 10% below their value at long times, and rise slowly with progressing time. On the other hand, the fibers from yarn start out some 25% lower than their long-time value, and rise fairly steeply during the first days of aging. This behavior is consistent with the hypothesis that the fibers from yarn are recovering some crimp which has been removed during the drawing occurring in spinning and which has been prevented from recovering while in the yarn because of the high degree of constraint within the twisted assembly.

Figure 13 shows the aging behavior of the crimp contraction, x. The values plotted are again arithmetic means for the 45 fibers in each set, normalized to their value at long aging times. The initial values for both the yarn and top are about half their final values at long aging times; the fibers from the yarn, however, show a more rapid change than the fibers from top. Again it appears that the yarn is recovering rapidly from the stretching action impressed during spinning.

Figure 14 shows the aging behavior of $F_o x/A$, a quantity more or less proportional to the crimp energy per unit volume of fiber material. The values plotted are derived from the data of Figures 12 and 13, and merely reflect the combined action of the recovery

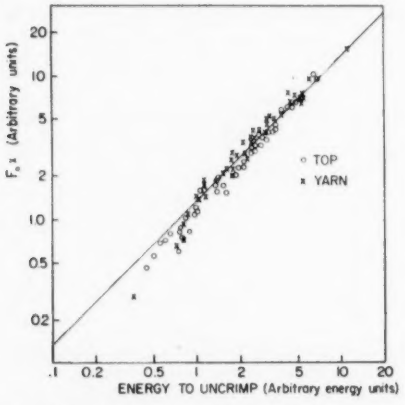

FIG. 11. *Scatter diagram for product of crimp stiffness times crimp contraction,* $F_o x$, *against energy to uncrimp,* E, *for single New Zealand medium wool fibers.*

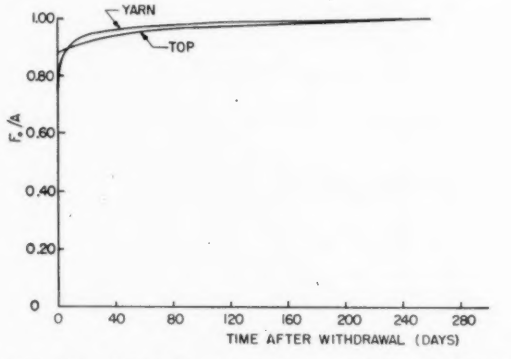

FIG. 12. *Variation of average crimp "stiffness,"* F_o/A, *with time after withdrawal from assembly, for sets of single New Zealand medium wool fibers from top and unsteamed yarn.*

of stiffness and contractive ability. Fibers from both the top and yarn recover much of their crimp energy with aging free from constraint, those from yarn showing the steeper rise.

In another experiment it was attempted to find the effect of steaming the yarn. The results indicated a smaller degree of crimp recovery in the steamed yarn, as evidenced with all three crimp parameters. This finding is interpreted as a setting of the fibers into their new less crimped configuration within the yarn.

Although it is likely that the dynamical parameters of crimp can be correlated with the geometrical parameters as measured optically, no such study has yet been made. The present study is to be considered only as an introduction to the behavior of wool during uncrimping.

The aging effects found in test *T-2* were observed in fibers that were allowed to age in an unconstrained configuration. Fibers were also withdrawn from the assemblies after varying periods of constrained aging *within* the assembly. The number of fibers studied, however, was too small to determine whether the fibers withdrawn after aging within the assembly undergo a degree of crimp recovery different from fibers aged outside the assembly. The only evidence we have for the absence of changes in physical properties—other than those pertaining to crimp—during aging outside the assembly is the failure of the Hookean slopes measured in test *T-2* to undergo any pronounced change. For in test *T-1*, to break, the fibers were all aged within the assembly, and then tested at approximately 2 days after withdrawal.

Heterogeneity within Samples

At each processing stage the samples of wool for test *T-1* were selected to allow estimates to be made as to the degree of blending achieved, and as to the extent to which mechanical and chemical treatments in various processing units affect the physical properties of the fibers.

In the grease stage the sampling was as follows: four times for each master wool, three staples at each time, two groups from each staple, and four fibers from each group. The data for the 96 fibers so selected for each of the master wools were treated by analysis of variance to determine whether all the fibers of a given wool could reasonably have been drawn from a single population of fibers, or whether fibers closely associated in a given staple tend to be more similar in their properties than fibers drawn from a group of staples. It was found that fibers from a given staple tend to be somewhat more uniform in diameter, elastic modulus, stress at 20% extension, and breaking extension than fibers from a group of staples. Since a large number of fleeces were included in the lots of wool processed, each staple selected was probably from a different sheep, and it is likely that the differences in properties between staples are really due to differences between individual sheep. The sheep-to-sheep differences in fineness have been quite thoroughly studied by Pohle and collaborators [5, 6]; the differences in mechanical properties have not been investigated previously. These differences will be considered more thoroughly in a later paper based on data derived from more suitable samples.

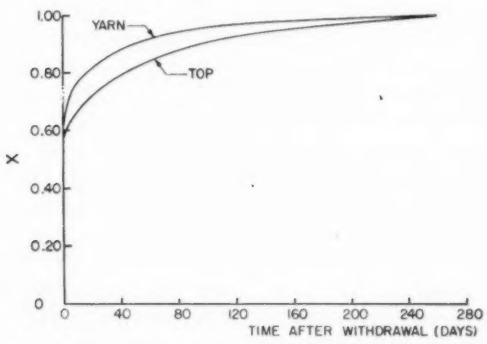

FIG. 13. *Variation of average crimp "contraction," x, with time after withdrawal from assembly, for sets of single New Zealand medium wool fibers from top and unsteamed yarn.*

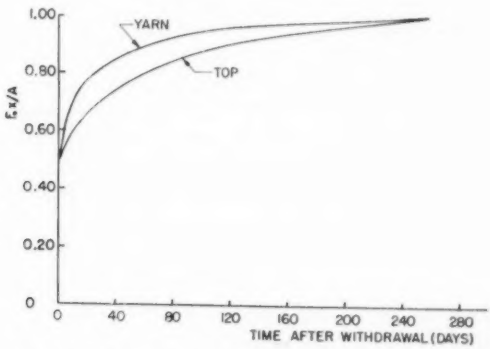

FIG. 14. *Variation of average crimp "energy," Fx/A, with time after withdrawal from assembly, for sets of single New Zealand medium wool fibers from top and unsteamed yarn.*

TABLE I. AVERAGE VALUES OF PHYSICAL PROPERTIES OF SINGLE WOOL FIBERS

Processing stage	Diameter (μ)				Elastic modulus (10^6 g./cm.^{2})				Stress at 20% extension (10^6 g./cm.^{2})			
	Aust. fine	U. S. fine	U. S. med.	N. Z. med.	Aust. fine	U. S. fine	U. S. med.	N. Z. med.	Aust. fine	U. S. fine	U. S. med.	N. Z. med.
Grease	22.7	24.6	28.5	29.2	23.2	22.2	24.1	25.4	0.91	0.88	0.94	0.91
Scoured	18.8	22.0	24.7	24.0	31.5	28.0	30.8	32.3	0.99	1.01	1.05	1.06
Top	19.3	21.6	25.8	27.1	30.8	29.1	30.9	35.1	1.05	1.06	1.09	1.18
Roving	19.5	21.7	26.0	26.8	32.7	30.4	33.0	36.8	1.08	1.07	1.13	1.16
Unsteamed yarn	19.9	—	26.5	27.4	36.1	—	34.1	36.9	1.12	—	1.17	1.17
Steamed yarn	—	21.5	25.9	27.9	—	39.4	38.2	36.6	—	1.13	1.18	1.16
Grey cloth	19.4	22.4	25.9	26.5	39.0	34.2	37.4	40.3	1.10	1.02	1.18	1.22
Ready-to-dye cloth	18.9	21.9	26.6	26.9	35.6	32.6	33.4	36.4	1.06	1.04	1.11	1.17
Finished cloth	20.0	23.1	28.3	28.8	34.3	31.6	32.4	33.6	1.00	0.99	1.08	1.12
Ave. coeff. of variation (%)	14.2	12.5	13.3	15.1	14.9	13.1	14.8	15.3	6.2	5.0	5.8	6.9

The scoured wool retains the heterogeneity of the grease wool to the extent that the original staples remain associated. Throughout the succeeding stages of processing from top to finished cloth, the samples indicated that the blending was adequate. There was no evidence from the physical properties that fibers passing through specific machines were more harshly handled than others. The investigation of staple length, however, might provide a more sensitive indication of mechanical damage in operations such as carding, gilling, and drawing.

Effects of Processing on Physical Properties

Tests at 65% R.H.—At selected stages in processing, one or more samples of 48 fibers each were tested. Since the changes during aging of the physical properties derived from test *T-1* were very small, as mentioned earlier, all of these tests could be used to evaluate the differences between wools and between processing stages. The average values at 65% R.H. of the six properties measured are listed in Table I. This table includes the average coefficients of variation for the selected samples used in this study.

The data for top, roving, and yarn were obtained on a series of days, and an unexplained day-to-day testing effect occurred. Consequently, a strict statistical comparison of the data in Table I necessitates some examination, and the daily averages were studied in a series of analyses of variance. In the Appendix is given an example of one of these analyses, together with a discussion on assessing the significance of differences between stages and between wools.

With the exception of the grease wool fibers, there was no indication that the fibers selected from various stages in processing were of different average diameter. The diameters given for grease wool are high because of the weight of the grease on the fibers. This bias is reflected in low values for those physical properties involving area in their calculation (k/A, F_{20}/A, and F_B/A).

The elastic modulus of all four wools exhibits a pronounced increase between the scoured state and steamed yarn, and an almost equal drop in the cloth stages. The apparent difference in modulus between grease and scoured wool is attributable to the area bias of the grease wool fibers.

The behavior of the stress at 20% extension through processing parallels very closely that of the elastic modulus. The small differences in the changes between the four wools are probably of little importance.

The relative energy for 20% extension ($E_{20}/0.20F_{20}$) shows very little tendency for change through processing. That is, the *shape* of the force-extension curve remains the same, although the force itself at a given extension tends to increase and then decrease as the fibers pass through processing, as shown by the behavior of the modulus and the stress at 20% extension.

The stress at break exhibits the same increase through the yarn stage and subsequent decrease during finishing as are observed for the elastic modulus and the stress at 20% extension. However, part of the change in breaking stress is a reflection of the extension at which break occurs. There is a definite increase in the extension at break between grease wool and top, and a pronounced drop between grey and finished cloth.

Tests in Water.—Following completion of the aging studies in air at 70°F and 65% R.H., a smaller

TABLE I. (*continued*)

Processing stage	Relative energy for 20% extension (%)				Stress at break (10^6 g./cm.^{2})				Extension at break (%)			
	Aust. fine	U. S. fine	U. S. med.	N. Z. med.	Aust. fine	U. S. fine	U. S. med.	N. Z. med.	Aust. fine	U. S. fine	U. S. med.	N. Z. med.
Grease	80.6	80.8	81.3	81.3	1.04	1.06	1.16	1.08	27.4	31.0	32.7	30.2
Scoured	81.3	82.5	81.8	80.8	1.27	1.19	1.28	1.26	33.0	26.7	30.6	28.9
Top	80.4	82.2	82.0	82.1	1.34	1.38	1.44	1.55	32.7	33.0	34.2	34.2
Roving	81.7	82.1	82.1	82.8	1.41	1.40	1.49	1.52	33.7	33.4	34.1	34.2
Unsteamed yarn	81.0	—	81.2	81.5	1.44	—	1.57	1.58	32.5	—	34.3	34.9
Steamed yarn	—	83.9	83.5	81.7	—	1.45	1.55	1.60	—	31.9	34.1	35.4
Grey cloth	82.6	84.9	82.2	83.0	1.37	1.36	1.47	1.58	31.1	34.2	30.6	33.7
Ready-to-dye cloth	81.4	83.2	82.7	81.5	1.22	1.30	1.46	1.52	27.4	30.7	34.2	33.3
Finished cloth	83.1	85.5	84.7	84.8	1.08	1.09	1.17	1.23	24.4	25.1	24.4	26.1
Ave. coeff. of variation (%)	4.4	3.1	4.2	4.7	16.5	17.5	17.7	17.9	24.6	29.4	27.0	25.6

TABLE II. PHYSICAL PROPERTIES OF U. S. MEDIUM WOOL IN WATER AT 70°F

Processing stage	D (65% R.H.) (μ)	k/A (10^6 g./cm.^{2})	F_{20}/A (10^6 g./cm.^{2})	$E_{20}/0.20F_{20}$ (%)	F_B/A (10^6 g./cm.^{2})	e_B (%)
Grease	30.4	15.2	0.52	80.0	1.39	49.4
Scoured	28.8	11.9	0.49	77.8	1.42	53.3
Top	26.7	13.2	0.48	77.7	1.33	51.6
Roving	26.3	12.3	0.47	77.6	1.25	50.0
Unsteamed yarn	27.7	12.3	0.48	77.1	1.24	48.9
Steamed yarn	26.4	15.1	0.50	79.2	1.28	49.0
Grey cloth	27.8	14.5	0.49	79.9	1.34	52.0
Ready-to-dye cloth	28.5	12.3	0.48	78.0	1.19	46.9
Finished cloth	25.4	10.0	0.36	77.7	0.82	45.4
Ave. coeff. of variation (%)	14.9	19.0	8.5	3.8	20.2	12.8

number of fibers of the U. S. medium wool from various stages of processing were tested in distilled water at 70°F. Eighteen fibers from each of the stages between grease wool and finished cloth were studied, six from each point being tested on each of 3 days. Area determinations were made in air with the vibroscope. The grease wool fibers were cleaned with alcohol and ether in a Soxhlet extractor. The data are listed in Table II.

The decrease in modulus, stress at 20% extension, and breaking stress through the cloth stages are more pronounced in water than in air. There is some evidence for a drop in wet modulus during scouring, but little indication of the progressive increases between scoured wool and grey cloth which were observed in air. Only the modulus appears to reflect this behavior. A small decrease in breaking extension occurs during the cloth stage.

Comparisons between Wools

Differences between the wools at corresponding points in processing are relatively slight. In general, the elastic modulus, stress at 20% extension, stress at break, and the breaking extension are all slightly higher for the medium wools than for the fine wools. Inasmuch as any small bias in the vibroscope determination of cross-sectional area is directly reflected in the modulus and stress determinations, these quantities may be in error to the extent of the uncertainty in area. Since no attempt was made to correct the cross-sectional areas for stiffness, the precise differences in these physical properties between wools cannot be definitely established, although they are certainly small.

The values for the breaking extensions of the fibers are free from this uncertainty, since the determination of the physical property itself is not affected by the bias in cross-sectional area. Therefore, the relationship between breaking extension, e_B, and fiber diameter, D, has been studied for the fibers from top, roving, and yarn for the four wools. Within each wool the constants were determined for an equation of the form

$$(e_B - \bar{e}_B) = b(D - \bar{D}).$$

The results are listed in Table III.

There is a definite tendency for the larger fibers in each wool type to have a higher extension at break than the smaller fibers, as shown by the positive values of the regression coefficient, b. Although there is an indication that the individual regression coefficients may be different, an average value of 0.310 ± 0.075 was calculated for the four wools. With this figure the breaking extensions at the over-all average diameter of 24.07 μ were calculated for the four wools. These are as follows:

	e_B at $D = 24.07\ \mu$
Aust. fine	33.89%
U. S. fine	33.85%
U. S. med.	33.56%
N. Z. med.	33.66%

All four values are well within the experimental error, and the average breaking extensions of all four wools, whether as top, roving, or yarn, tend to cluster about the line

$$e_B = 0.310\ D + 26.08.$$

Part III: Summary and Conclusions

Physical properties of single wool fibers withdrawn at various points in worsted processing have been studied for four master wools (Merino 70's, Rambouillet 64's, Targhee 58's and Corriedale 58's). The following properties, obtained from force-extension curves to break, were measured at 65% R.H. and in water: Hookean slope, force at 20% extension, energy for 20% extension, force at break, and extension at break. Repetitive extensions to the end of the Hookean region were made on fibers from top, roving, and yarn in order to study low-extension parameters during aging at these stations.

On a unit cross-sectional area basis the force-extension curves of different fibers from the same source are very similar, although larger fibers appear to have slightly higher average values of the force per unit area at any extension, and to have somewhat higher extensions at break at 65% R.H. Throughout processing the four wools studied exhibited, in general, very similar changes in physical properties. At 65% R.H. an increase of 10% to 20% took place in Hookean slope, force at 20% extension, breaking force, and breaking extension between the scoured wool stage and steamed yarn. An approximately equal decrease in these properties occurred between grey cloth and finished cloth. When the fibers are tested in water, the decrease during the cloth stages is even more apparent, but the other changes observed at 65% R.H. do not appear. At the same extension, the force in water is only about 40% of that at 65% R.H. The breaking force, however, is not very much lower, the breaking extension in water being considerably greater than at 65% R.H. The general shape of the force-extension curve is essentially the same for all the fibers tested, both in air and in water.

The physical properties characteristic of the high-extension region of the force-extension curve do not change appreciably during an aging period following gilling, drawing, or spinning. The low-extension region, however, gives evidence of a return of crimp during a period of unconstrained aging following these operations.

TABLE III. REGRESSION OF BREAKING EXTENSION ON DIAMETER

Wool	$\bar{D}$ (μ)	e_B (%)	b (μ/%)	Residual variance	No. of fibers
Aust. fine	19.49	32.32	0.36 ± 0.27	75.9	516
U. S. fine	21.65	32.94	0.20 ± 0.21	94.7	1098
U. S. med.	25.97	33.99	0.19 ± 0.14	86.0	1382
N. Z. med.	27.11	34.45	0.42 ± 0.10	75.3	1531

Appendix

It was mentioned earlier (p. 698) that analysis of variance is called for in the examination of the data.

TABLE IV. ANALYSIS OF VARIANCE FOR U. S. MEDIUM WOOL (DAILY AVERAGES FOR 48 FIBERS)

	Diameter (μ)		
	Top	Roving	Yarn
	24.9	26.6	24.6
	25.0	25.2	26.0
	27.9	24.9	26.4
	25.0	25.6	25.9
	25.3	26.7	27.2
	25.5	27.0	27.4
	25.5	26.5	26.4
	26.2	25.3	26.6
	25.8	25.8	
	26.7		
Ave.	25.8	26.0	26.3

	Degrees of freedom	Sum of squares	Mean square	F
Between processing stages	2	1.28	0.64	
Between days	24	17.79	0.741	2.98**
Within days (see Table V)	~1300		0.248 (for means of 48)	

TABLE V. RESULTS FROM ANALYSIS OF VARIANCE FOR PHYSICAL PROPERTIES OF SINGLE FIBERS

		D (μ)	k/A (10^6 g./cm.^{2})	F_{20}/A (10^4 g./cm.^{2})	$E_{20}/0.20F_{20}$ (%)	F_B/A (10^4 g./cm.^{2})	e_B (%)	Approximate degrees of freedom
s_o^2	Aust. fine	0.160	0.498	1.04	0.236	10.9	1.32	400
	U. S. fine	0.151	0.400	0.62	0.148	12.8	1.95	900
	U. S. med.	0.248	0.533	0.99	0.231	14.9	1.76	1300
	N. Z. med.	0.347	0.646	1.48	0.290	16.5	2.16	1400
s_d^2		0.3216	1.3056	9.936	0.5472	5.136	0.4464	60

An example is given here of such an analysis on a typical property—the diameter of single fibers. A discussion then follows on assessing the significance of the observed differences.

The highly significant between-days result is the daily testing effect referred to above. Because of its presence, the standard deviation of a processing stage average is $(0.741/n)^{1/2}$, where n is the number of days, and *not* $(0.248/n)^{1/2}$, which would be the estimate of error in the absence of any difference between days. The effect was observed in all the properties measured with the exception of the extension at break. Attempts, all unsuccessful, were made to determine its source through plots of daily averages of physical properties against diameter (to detect a possible daily bias in the diameter measurements), original fiber length, vibroscope tensioning weight, and relative humidity in the narrow range present in the conditioned room in which the tests were performed.

In Table IV the between-days mean square, equal to 0.741, is an estimate of $\sigma_o^2 + \sigma_d^2$ with 24 degrees of freedom. The error variance, σ_o^2, is estimated by the within-days mean square, 0.248. From similar analyses of variance for the other three master wools, three more estimates of σ_d^2 were obtained. The pooled estimates are listed in Table V as well as the estimates of the variance of a mean derived from 48 fibers (s_o^2). Variances of the means given in Table I can be synthesized by the equation

$$s_{\bar{X}}^2 = (1/n)\,[(48s_o^2/m) + s_d^2],$$

where m is the number of fibers tested per day, and n is the number of different days on which tests were conducted. The number tested per day was 48 for all samples except the medium wool yarns, for which it was 24. The number of testing days for each processing stage for each wool is listed in Table VI.

TABLE VI. NUMBER OF TESTING DAYS FOR MASTER WOOL SAMPLES

Processing stage	Aust. fine	U. S. fine	U. S. med.	N. Z. med.
Grease	2	2	2	2
Scoured	1	1	1	1
Top	3	7	10	10
Roving	3	7	9	10
Unsteamed yarn	3	—	10	10
Steamed yarn	—	6	10	10
Grey cloth	1	1	1	1
Ready-to-dye cloth	1	1	1	1
Finished cloth	1	1	1	1

With the estimates of error obtained by these procedures, the individual means of Table I were compared by Scheffé's method [7].

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The Plasticity of Wool
Part II: Variation with Type of Follicle*

R. W. Burley and J. B. Speakman

Textile Chemistry Laboratory, Department of Textile Industries, The University, Leeds, England

Abstract

The variations in plasticity among the fibers of single staples of New Zealand Lincoln, New Zealand Romney, and Australian merino wools are associated with follicles of different types and ages. Primary follicles produce fibers of lower plasticity than those of secondary follicles, and the order of plasticity of the fibers is, in general, the inverse of the order of development of the follicles.

IN its later stages the extension of wool fibers under constant load in water at 22.2°C is represented by a linear relationship when log $(E - E_t)$ is plotted against t, where E is a limiting extension and E_t is the extension at time t. The slope k of the line gives a convenient measure of plasticity, and values ranging from 3.83×10^{-5} to 50.2×10^{-5} have been obtained for fibers taken from a single lock of English Lincoln wool, extensions being expressed as percentages and times in minutes [3]. Similar variations in plasticity have since been observed with fibers taken from single locks of other wools and mohair [4]. The purpose of the present investigation was to discover their origin.

It seemed possible that the differences in plasticity might be associated with follicles of different types and ages. The first follicles to develop in the unborn lamb are termed "primary central" follicles, which can sometimes be recognized by their large size. Soon afterwards, "primary lateral" follicles grow at the sides of the primary central follicles, forming groups of three. Each primary follicle is associated with three accessory organs—an arrector pili muscle, a sudoriferous gland, and a sebaceous gland—but the later "secondary follicles," which develop near the primary triads, have either no accessory organs or only sebaceous glands. The secondary follicles arise in waves, beginning before birth and continuing after birth. They are always more numerous than the primaries, but the ratio of primary to secondary follicles varies with the breed of sheep and, to a lesser extent, the age of the animal. In the merino fleece, for example, the secondaries may be thirty times as numerous as the primaries, whereas there are usually only two to three times as many secondaries as primaries in New Zealand Romney fleeces [1].

It would, of course, be difficult to discover whether there is any relationship between the plasticity of fibers and the types of follicle from which they are derived without some means of identifying the sources of the fibers in shorn wool. Fortunately, a scheme of identification for hogget's wool has been evolved by Dr. F. W. Dry and his colleagues in New Zealand [2]. Following up an observation of the late Professor J. E. Duerden, they have been able to show that fibers from different types of follicles have tips of different shapes. If, in addition, account is taken of the state of medullation of the tip and the immediate postnatal region, as well as of a factor known as the "prenatal check," which has a marked effect on the formation of those fibers which started growing before the birth of the lamb, and if the lengths of the fibers are noted, it is possible to classify fibers according to both the order of appearance and the type of the follicle.

The main types of fiber in Dry's classification are given below in the order of their appearance in the fleece, and a photograph of the types present in a New Zealand Lincoln wool is reproduced in Figure 1.

Fibers from Primary Central Follicles

Halo-hairs, so-called because they project above the rest of the fibers in the coat of the newly born

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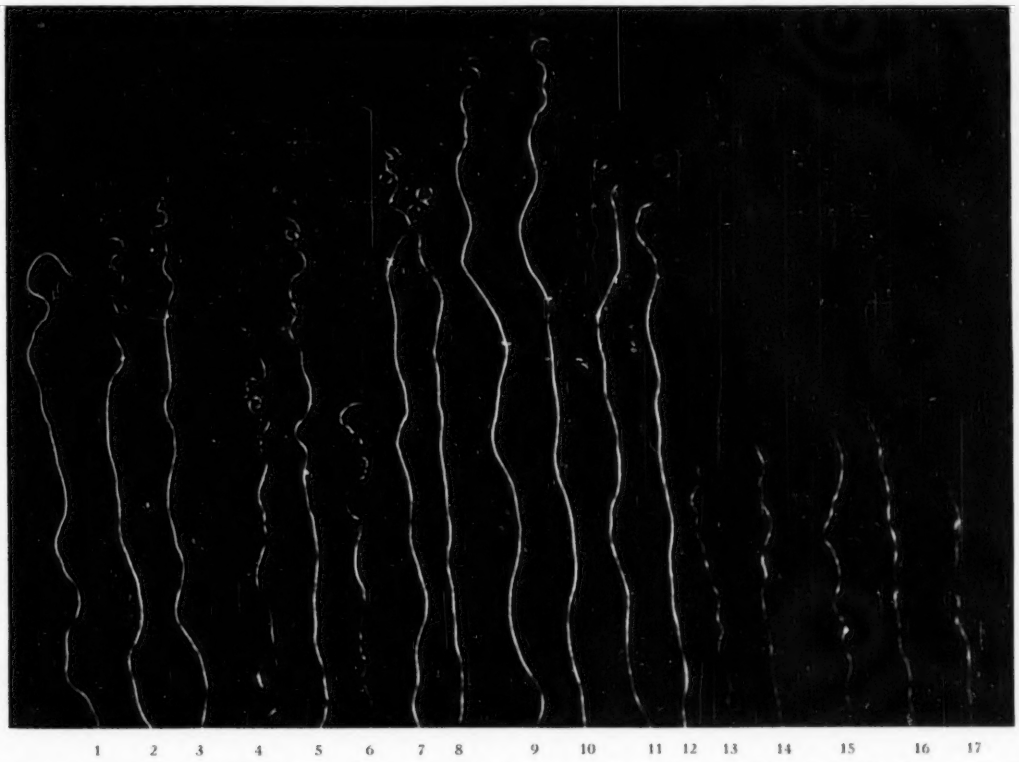

Fig. 1. *Types of fiber present in a New Zealand Lincoln wool.* 1—*Super-sickle.* 2, 3—*Sickles.* 4, 5—*Fine sickles.* 6—*Very fine sickle.* 7, 8—*Curly-tips (checked).* 9, 10—*Curly-tips (peak).* 11, 12—*Curly-tips (late).* 13–17—*Histerotrichs.*

lamb; the fibers are heavily medullated and are usually shed a few months after birth.

Super-sickles, with medullated, sickle-shaped tips, which are much larger than the tips of other fibers, except the halo-hairs. According to the state of medullation of the tip and the immediate postnatal region, the super-sickles may be allotted to subtypes *A, A′,* and *B.* In type *A* the fibers are continuously medullated throughout the prenatal and postnatal regions. Fibers of type *A′* show a break in medullation at birth, while those of type *B* have discontinuous medullation before birth and a break at birth.

Sickles, which have two characteristics—*viz.,* a thick, sickle-shaped end, which may be medullated and should taper towards the tip, and a much thinner "neck region" having many small curls. This region extends from the base of the sickle-shaped end to the "birth point," after which the fiber is thicker and straighter.

Fibers from Primary Lateral Follicles

Hairy-tip-curly-tips.—These have a heavily medullated initial curl, which is larger than that of the normal curly-tips; they can be distinguished from super-sickles by the fact that the initial curl is usually slightly smaller and more circular.

Early curly-tips.—The tips, which have several curls, show no marked thickening or taper and are not usually medullated.

Fibers from Secondary Follicles

Late curly-tips.—The fibers are similar to the early curly-tips, except that the tips have fewer curls.

Histerotrichs.—These start growing just before or after birth. The tips are either straight or, more generally, have a few minute curls or wriggles.

Fibers from various wools were classified according to the above scheme in the following attempt to discover whether variations in plasticity are associated with follicles of different types and ages.

Experimental Procedure

Purification of Wool

Most of the samples examined were obtained from Dr. F. W. Dry in New Zealand. For the purposes of his own work he had fitted the animals with canvas squares, which were attached to their backs with Bostik cement in order to protect the tips of the fibers. Each sample of wool was purified by extraction in a Soxhlet apparatus with ether and alcohol for 24 hrs. each, followed by washing with frequent changes of distilled water over a period of 24 hrs. After the wool had been pressed between filter papers, it was allowed to dry in room air, and the fibers were then classified according to Dry's scheme. Certain of the samples, which had been sorted into various types by Dr. Dry, were purified after classification.

Calibration of Fibers

In all cases except one, the fibers were nonmedullated, and measurements of plasticity were made on the intact root ends. A 5-cm. length of fiber was attached to light glass hooks by means of polymethylmethacrylate, which was applied as a concentrated solution in a mixture of chloroform and carbon tetrachloride. The cross-sectional area of the fiber was then estimated by making diameter measurements, after overnight conditioning in a room maintained at 65% relative humidity and 22.2°C, so that the load to be used in determinations of plasticity could be calculated. With fibers of reasonably uniform diameter and approximately circular cross section, such as those of Lincoln wool, the diameter was measured at 25 places along the length. In the case of more irregular wools, diameter measurements were made at 50 places along the length, and occasional fibers which showed a systematic variation in diameter, such as tapering, were rejected. The coefficient of variation in diameter was calculated for each fiber in order to provide an indication of the extent to which variation in the rate of creep under load might be due to variation in the irregularity of cross-sectional area. It should be noted, however, that the coefficient of variation of diameter is greater than that of cross section, because the fibers are only approximately circular in cross section.

Before being used for plasticity measurements, some of the fibers were characterized by determining treatment, and the work required for 30% extension, distilled water at 22.2°C by means of the Cambridge Fiber Extensometer. It has already been shown [3] that the plasticity of wool fibers is not affected by this treatment, and the work required for 30% extension, which can be calculated from the load-extension curve, was intended for comparison with plasticity.

Determination of Plasticity

The plasticity of the fibers was determined by allowing them to extend in distilled water at 22.2°C under a load which was usually 700 kg./cm.^{2} In order to eliminate possible errors due to slight differences in friction of the pulleys used to transmit load to the fibers in earlier work [3], the fibers were loaded directly. For this purpose, the open end of a glass tube, 35 cm. long by 4 cm. diameter, was ground flat at right angles to the length. After the tube had been filled with distilled water and mounted in a thermostat, a strip of Perspex was placed across the open end and the fiber was suspended from it by means of a nylon thread, which was tied to the upper hook. A light glass weight, just sufficient to draw the fiber taut, was then added to the lower hook, and the unstretched length of the fiber between tiny beads of Perspex near the upper and lower hooks was measured by means of a traveling microscope reading to 0.05 mm. The weight was then removed and replaced by a glass specimen tube, which was adjusted to the desired weight with fragments of glass rod, taking into account the buoyancy of water. Before being suspended from the fiber, the tube was, of course, filled with distilled water and the contents were stirred to remove air bubbles. From preliminary experiments, in which tubes containing glass rod were weighed in air and in water, it was found that the weight (in grams) required for a load of 700 kg./cm.^{2} was given by the formula

$$W = \frac{\pi d^2}{4} \times 7 \times 10^5 \times 1.670 = d^2 \times 9.182 \times 10^5,$$

where d is the average diameter of the fiber (in centimeters). The length of the fiber was measured at intervals until sufficient data had been obtained to allow the plasticity constant k to be evaluated by plotting log $(E - E_t)$ against t.

Results

Lincoln 770

Five locks taken from a standard position on the animal's back—on the middle line at the level of at-

tachment of the last rib—were sorted into fibers of various types; the results were as follows:

Super-sickles	5
Sickles	157
Early curly-tips	690
Late curly-tips	784
Long histerotrichs	1094
Short histerotrichs	589

Since the sickles and early curly-tips are derived from primary follicles and the late curly-tips and histerotrichs from secondary follicles [2], the ratio of primaries to secondaries at the end of the year was 1 : 2.90.

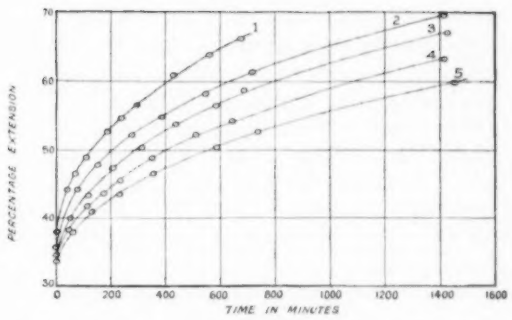

FIG. 2. *Typical extension-time curves for Lincoln 770 fibers. 1—Short histerotrich (no. 4). 2—Long histerotrich (no. 8). 3—Early curly-tip (no. 5). 4—Super-sickle (no. 1). 5—Sickle (no. 6).*

TABLE I. LINCOLN 770

Type of fiber	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-5}$)
Super-sickles	43.3	8.35	1.04	34.5	47.7
	40.1	8.26	1.34	34.8	53.8
	43.2	7.12	1.29	34.9	54.3
	40.2	6.75	1.11	36.7	73.7
	38.0	6.86	1.48	32.5	36.8
	41.0	*7.47*	*1.25*	*34.7*	*53.3*
	$sd = 2.0$		$sd = 0.15$		$sd = 12.0$
	$cv = 4.9\%$		$cv = 12.0\%$		$cv = 22.5\%$
			$pe = 0.08$		$pe = 6.0$
Sickles	35.5	6.80	1.44	33.4	27.1
	37.4	7.36	1.45	39.8	39.5
	38.6	6.40	1.36	33.9	37.5
	38.5	9.85	1.46	32.6	29.1
	42.0	6.37	1.42	33.2	34.1
	39.1	5.98		33.6	36.1
	43.9	9.52		34.6	41.4
	38.2	8.64		33.1	44.7
	34.9	7.57		37.0	67.3
	38.7	*7.61*	*1.43*	*34.6*	*39.6*
	$sd = 2.7$		$sd = 0.11$		$sd = 11.1$
	$cv = 7.0\%$		$cv = 7.9\%$		$cv = 28.0\%$
			$pe = 0.06$		$pe = 3.9$
Early curly-tips	44.2	9.62	1.33	34.9	52.3
	47.3	8.39	1.29	34.6	51.5
	42.9	6.45	1.41	34.2	57.0
	44.6	6.31	1.34	34.1	58.2
	42.6	10.00	1.44	34.6	61.0
	39.8	7.70	1.42	32.9	42.4
	43.7	12.89		35.1	85.5
	45.4	7.70		34.1	70.5
	36.2	6.31		32.6	57.0
	43.0	*8.37*	*1.37*	*34.1*	*59.5*
	$sd = 3.1$		$sd = 0.17$		$sd = 11.7$
	$cv = 7.2\%$		$cv = 12.6\%$		$cv = 19.7\%$
			$pe = 0.08$		$pe = 4.1$
Late curly-tips	38.4	6.95	1.28	34.6	60.0
	41.3	9.12	1.42	34.1	64.0
	43.4	5.58		34.2	57.0
	36.7	6.34		34.9	57.0
	33.3	7.17		33.8	57.0
	42.1	8.16	1.38	34.5	41.3
	41.5	6.52	1.43	34.9	56.8
	43.5	7.23	1.48	33.5	51.8
	34.1	8.51	1.23	36.9	79.3
	39.4	*7.29*	*1.37*	*34.6*	*58.2*
	$sd = 3.7$		$sd = 0.26$		$sd = 9.5$
	$cv = 9.3\%$		$cv = 18.7\%$		$cv = 16.3\%$
			$pe = 0.10$		$pe = 3.4$
Long histero-trichs	28.4	10.43		38.6	88.8
	33.2	9.71		37.8	99.0
	28.6	9.35		37.9	95.4
	28.6	10.70		36.3	71.5
	31.4	11.54		36.2	67.0
	26.8	6.92	1.09	38.8	63.4
	35.4	7.56	1.41	34.4	57.0
	34.5	8.82	1.29	35.7	70.5
	41.8	4.74	1.28	35.6	63.4
	32.1	*8.86*	*1.27*	*36.8*	*75.1*
	$sd = 4.4$		$sd = 0.11$		$sd = 14.4$
	$cv = 13.7\%$		$cv = 8.7\%$		$cv = 19.2\%$
			$pe = 0.07$		$pe = 5.1$
Short histero-trichs	26.2	9.56	1.20	broke	—
	23.8	5.91	1.08	39.1	56.6
	22.4	5.45	1.23	42.2	220
	27.4	8.74	1.26	37.8	122
	30.4	8.50		36.0	54.6
	28.1	8.24	1.11	42.9	213
	28.1	10.69	1.15	41.7	210
	26.5	13.00		40.5	220
	26.6	*8.76*	*1.17*	*40.0*	*157*
	$sd = 2.4$		$sd = 0.20$		$sd = 71.0$
	$cv = 8.9\%$		$cv = 17.3\%$		$cv = 45.4\%$
			$pe = 0.09$		$pe = 26.8$

From each group except the first, nine fibers were taken at random with tweezers. After the load-extension curves of four or more of the fibers had been determined, all the fibers were extended under a load of 700 kg./cm.^{2} in distilled water at 22.2°C. Typical extension-time curves for most types of fiber are shown in Figure 2. It was found that the best linear relationships between log $(E - E_t)$ and t were obtained when E was taken to be 70%, and the values of k given in Table I were obtained in this way. In the table, the average diameter of each fiber is given, and C.V. is the coefficient of variation of the diameter. Also given are the work, W, needed for a 30% extension, and E_1, the extension after 1 min. in the plasticity experiments. Average values are italicized. The standard deviation, *sd*, the coefficient of variation, *cv*, and the probable error, *pe*, are given where appropriate. The values of k are all negative, but the minus sign has been omitted for convenience in presenting the results.

Descaled Lincoln 770

Several fibers of three of the types present in Lincoln 770—*viz.*, sickles, early curly-tips, and long histerotrichs—were descaled before examination. For this purpose, each fiber was drawn between two pieces of emery paper (grade 1F) ten times in succession against the scales. Fibers of more than average coarseness were used in order to minimize the risk of breakage during descaling. Microscopic examination failed to reveal any traces of scale structure in the treated fibers, which were then examined in the usual way. The results are given in Table II.

TABLE II. DESCALED LINCOLN 770

Type of fiber	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-5}$)
Sickles	41.3	7.26	1.22	34.6	43.7
	36.3	8.18	1.39	34.9	35.9
	36.9	6.28	1.26	34.5	25.0
	41.0	6.41	1.66	33.3	28.0
	44.6	6.66	1.11	36.5	67.5
	40.0	*6.96*	*1.33*	*34.8*	*40.1*
Early curly-tips	37.8	8.99	1.35	33.2	57.6
	38.8	5.94	1.36	33.6	64.3
	44.2	10.19	1.45	34.2	61.5
	34.2	6.11	1.26	33.7	53.5
	39.8	*7.81*	*1.36*	*33.7*	*59.3*
Long histerotrichs	31.5	10.08	1.28	35.4	68.9
	29.5	11.29	1.04	40.1	173
	35.2	8.89	1.12	—	—
	31.3	7.85	1.40	35.8	92.6
	31.3	11.52	1.13	—	—
	31.6	9.50	1.28	36.7	69.5
	30.2	9.83	1.25	35.3	50.0
	34.5	6.31	1.42	34.9	70.0
	34.7	8.18	1.22	36.6	85.6
	41.5	7.47	1.18	—	—
	33.1	*9.09*	*1.23*	*36.4*	*87.1*

Lincoln 640, 752, and 772

Only one lock taken from the standard position on the sheep's back was used in each of these cases. Fibers were selected as required and tested in the same way as before. It seems unnecessary to record the results in as great detail as for Lincoln 770, and only average results are given in Table III. There are no data for super-sickles because a sufficient number of fibers of this type could not be found in any of the staples.

Lincoln Lamb's Wool

The sample, which was taken when the lamb was 6 months old, had been sorted into fibers of different types by Dr. Dry in New Zealand. Unlike the other groups, the "checked" and "peak" curly-tips were found to contain medullary islands, but the amount of medulla was small and the results are therefore included in Table IV.

New Zealand Romney Wool

Two samples of New Zealand Romney wool, subsequently referred to as "Romney 1" and "Romney 2," were sorted into fibers of different types by Dr. Dry. The samples were from the standard position on the backs of two sheep which had been covered 2 months after birth, and the fibers were selected from several staples in an area of not more than a few square inches of skin.

In the case of Romney 1, the sheep was 12 months old when the sample was taken. The fibers were thinner, more crimped, and, according to the coefficients of variation in diameter, more irregular than the Lincoln fibers. They broke so readily under a load of 700 kg./cm.^{2} that a load of 600 kg./cm.^{2} had to be used in plasticity measurements. Nevertheless, early breakages were common. A limiting extension of 50% was used in calculating the values of k given in Table V.

The Romney 2 samples, which was taken from a sheep 14 months old, had been preserved in a tightly closed metal box for 15 years before being sorted by Dr. Dry for these experiments. In explanation of

TABLE III

Type of fiber	No. of fibers examined	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-5}$)
Lincoln 640						
Sickles	9	*37.2*	*7.46*	*1.30*	*35.3*	*39.1*
		$sd = 3.0$ $cv = 8.0\%$		$sd = 0.05$ $cv = 3.8\%$ $pe = 0.03$		$sd = 8.5$ $cv = 21.7\%$ $pe = 3.0$
Early curly-tips	9	*39.9*	*8.32*	*1.37*	*34.7*	*55.0*
		$sd = 1.9$ $cv = 4.9\%$		$sd = 0.03$ $cv = 2.0\%$ $pe = 0.02$		$sd = 7.6$ $cv = 13.8\%$ $pe = 2.7$
Late curly-tips	7	*37.7*	*6.93*	*1.25*	*35.4*	*96.2*
		$sd = 0.8$ $cv = 2.1\%$		$sd = 0.09$ $cv = 7.6\%$ $pe = 0.05$		$sd = 13.5$ $cv = 14.0\%$ $pe = 5.5$
Long hetero-trichs	9	*31.7*	*7.43*	*1.25*	*36.7*	*106*
		$sd = 3.6$ $cv = 11.4\%$		$sd = 0.03$ $cv = 2.1\%$ $pe = 0.02$		$sd = 10.4$ $cv = 9.8\%$ $pe = 3.7$
Short hetero-trichs	8	*25.1*	*7.02*	*1.11*	*38.0*	*109*
		$sd = 2.5$ $cv = 10.1\%$		$sd = 0.11$ $cv = 10.3\%$ $pe = 0.06$		$sd = 13.0$ $cv = 11.9\%$ $pe = 4.9$
Lincoln 752						
Sickles	9	*36.2*	*6.83*	*1.41*	*34.5*	*60.3*
		$sd = 1.0$ $cv = 2.8\%$		$sd = 0.13$ $cv = 9.2\%$ $pe = 0.07$		$sd = 5.7$ $cv = 9.5\%$ $pe = 2.2$
Early curly-tips	9	*39.8*	*8.75*	*1.36*	*35.4*	*66.2*
		$sd = 1.6$ $cv = 4.0\%$		$sd = 0.25$ $cv = 18.6\%$ $pe = 0.13$		$sd = 6.8$ $cv = 10.3\%$ $pe = 2.6$
Late curly-tips	8	*34.8*	*7.94*	*1.30*	*37.0*	*81.7*
		$sd = 3.5$ $cv = 10.1\%$		$sd = 0.16$ $cv = 12.4\%$ $pe = 0.08$		$sd = 18.0$ $cv = 22.0\%$ $pe = 6.8$
Long hetero-trichs	9	*31.3*	*8.09*	*1.23*	*39.0*	*120*
		$sd = 2.2$ $cv = 6.9\%$		$sd = 0.06$ $cv = 4.9\%$ $pe = 0.03$		$sd = 4.8$ $cv = 2.5\%$ $pe = 1.8$
Short hetero-trichs	10	*24.0*	*7.91*	*1.13*	*40.0*	*134*
		$sd = 1.9$ $cv = 7.9\%$		$sd = 0.21$ $cv = 18.3\%$ $pe = 0.11$		$sd = 29.5$ $cv = 22.0\%$ $pe = 10.4$
Lincoln 772						
Sickles	9	*40.1*	*7.40*	*1.38*	*34.7*	*56.1*
		$sd = 2.2$ $cv = 5.4\%$		$sd = 0.14$ $cv = 10.3\%$ $pe = 0.07$		$sd = 5.4$ $cv = 9.7\%$ $pe = 1.9$
Early curly-tips	9	*44.7*	*8.23*	*1.27*	*35.8*	*68.6*
		$sd = 1.5$ $cv = 3.4\%$		$sd = 0.22$ $cv = 17.1\%$ $pe = 0.11$		$sd = 14.4$ $cv = 20.9\%$ $pe = 5.1$
Late curly-tips	9	*39.7*	*7.10*	*1.27*	*36.9*	*74.1*
		$sd = 2.6$ $cv = 6.6\%$		$sd = 0.24$ $cv = 18.6\%$ $pe = 0.12$		$sd = 11.5$ $cv = 15.5\%$ $pe = 4.1$
Long hetero-trichs	9	*35.2*	*8.09*	*1.34*	*37.7*	*90.4*
		$sd = 3.2$ $cv = 9.2\%$		$sd = 0.29$ $cv = 21.5\%$ $pe = 0.14$		$sd = 13.0$ $cv = 14.4\%$ $pe = 4.9$
Short hetero-trichs	8	*26.7*	*7.69*	*1.18*	*39.0*	*106*
		$sd = 2.3$ $cv = 8.6\%$		$sd = 0.38$ $cv = 31.8\%$ $pe = 0.19$		$sd = 53.4$ $cv = 50.3\%$ $pe = 21.8$

Dry's classification, it should be noted that the "chalky sickles" were medullated for about 2 in. after birth, and that the descriptions "fine" and "finer," applied to the sickles, refer to diameters in the postnatal region. The four groups of curly-tips have progressively fewer curls in the prenatal tip, and are progressively finer in the postnatal region. A load of 700 kg./cm.^{2} was used in plasticity measurements, and the values of k given in Table V were calculated with a limiting extension of 60%. No anomalies due to the long period of storage of the wool were detected.

Australian Merino Lamb's Wool

A long staple was selected from the back of a 70s Australian merino fleece. Although the sheep had not been covered to prevent damage to the tips of

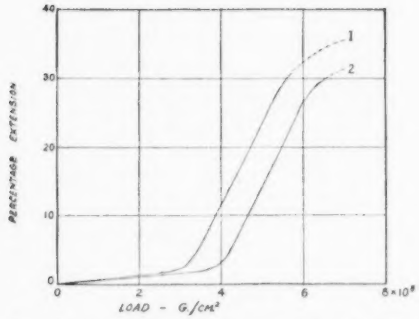

FIG. 3. *Typical load-extension curves for Lincoln 770 fibers.* 1—*Long histerotrich.* 2—*Sickle.*

fibers, the tips were fairly well preserved and easy to identify. After purification, the staple was sorted into sickles, curly-tips with many curls, and histerotrichs, the sickles being, of course, very rare. A load of 700 kg./cm.^{2} was used in plasticity measurements, and the values of k given in Table VI were obtained with a limiting extension of 75%.

Discussion

The average values for the work required to stretch fibers 30% are given in Table VII for all the samples tested. Where the samples were sorted by Dr. Dry, the values for the subsidiary types have been averaged and allotted to one of the five principal types so as to fit in with the classification of the others.

Typical load-extension curves for the sickles and long histerotrichs of Lincoln 770 are reproduced in Figure 3, the corresponding values for the work for 30% extension being 1.46×10^5 g.cm.$^{-2}$ and 1.28×10^5 g.cm.$^{-2}$ These show that the differences in resistance to extension are not associated with changes in form of the load-extension curve, but are due simply to the fact that unfolding of the main chains begins at different energy levels with different fibers. In general, the greatest resistance to extension is shown by the sickles and the least by the short histerotrichs, but there are exceptions to this rule, and it is evident that for intermediate types there is no simple relationship between the resistance to extension and the kind of follicle from which the fiber is derived.

The differences in plasticity among different types of fiber from the same wool, and samples of the same type from different wools, are very much greater than the differences in work for 30% extension, as may be seen from the data of Tables I, III, IV, V, and VI. With few exceptions, there is a progressive increase in the value of k from sickles to short histerotrichs, although the difference between adjacent groups is not always significant. For example, the difference between sickles and early curly-tips is significant at the 5% level, according to the t-test, for samples 772, 770, and 640 ($P = 0.01$, < 0.01, and < 0.001, respectively), but not for sample 752 ($P = 0.07$); and there is no significant difference

TABLE IV. LINCOLN LAMB'S WOOL

Type of fiber	No. of fibers examined	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-8}$)
Sickles	5	*37.0*	*7.40*	*1.30*	*35.5*	*20.3*
		$sd = 1.2$ $cv = 3.3\%$		$sd = 0.03$ $cv = 2.3\%$ $pe = 0.02$		$sd = 5.6$ $cv = 27.6\%$ $pe = 2.8$
Fine sickles	12	*35.5*	*6.84*	*1.32*	*34.0*	*22.2*
		$sd = 2.8$ $cv = 7.9\%$		$sd = 0.08$ $cv = 5.8\%$ $pe = 0.04$		$sd = 3.6$ $cv = 16.2\%$ $pe = 1.1$
Checked curly-tips	14	*38.7*	*7.55*	*1.09*	*36.8*	*16.0*
		$sd = 2.3$ $cv = 5.9\%$		$sd = 0.08$ $cv = 7.9\%$ $pe = 0.04$		$sd = 5.5$ $cv = 34.4\%$ $pe = 1.5$
Peak curly-tips	15	*42.6*	*9.44*	*1.09*	*37.0*	*18.7*
		$sd = 1.8$ $cv = 4.2\%$		$sd = 0.06$ $cv = 5.0\%$ $pe = 0.02$		$sd = 5.5$ $cv = 29.4\%$ $pe = 2.5$
Late curly-tips	17	*35.2*	*7.65*	*1.09*	*36.8*	*35.8*
		$sd = 2.3$ $cv = 6.4\%$		$sd = 0.06$ $cv = 5.0\%$ $pe = 0.02$		$sd = 10.0$ $cv = 27.9\%$ $pe = 2.5$
Long histero-trichs	8	*26.3*	*7.77*	*1.19*	*40.6*	*35.0*
		$sd = 2.0$ $cv = 7.6\%$		$sd = 0.06$ $cv = 5.2\%$ $pe = 0.02$		$sd = 5.3$ $cv = 15.1\%$ $pe = 2.4$
Medium histero-trichs	13	*29.8*	*7.37*	*1.13*	*37.6*	*41.6*
		$sd = 2.6$ $cv = 8.9\%$		$sd = 0.06$ $cv = 5.1\%$ $pe = 0.02$		$sd = 2.8$ $cv = 6.7\%$ $pe = 0.8$
Short histero-trichs	7	*25.0*	*8.13*	*1.03*	*39.2*	*38.8*
		$sd = 0.5$ $cv = 1.8\%$		$sd = 0.06$ $cv = 6.2\%$ $pe = 0.02$		$sd = 3.2$ $cv = 8.3\%$ $pe = 1.8$

TABLE V

Type of fiber	No. of fibers examined	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-5}$)
Romney 1						
Fine sickles	9	*25.6*	*10.37*	*1.42*	*32.1*	*68.6*
		$sd = 1.8$		$sd = 0.05$		$sd = 8.8$
		$cv = 7.0\%$		$cv = 3.2\%$		$cv = 12.8\%$
				$pe = 0.02$		$pe = 5.1$
Curly-tips (many small curls)	7	*29.9*	*12.33*	*1.26*	*32.5*	*86.9*
		$sd = 2.7$		$sd = 0.08$		$sd = 24.7$
		$cv = 9.2\%$		$cv = 6.2\%$		$cv = 28.4\%$
				$pe = 0.06$		$pe = 10.0$
Curly-tips (many large curls)	13	*31.6*	*12.24*	*1.21*	*34.8*	*100*
		$sd = 5.0$		$sd = 0.09$		$sd = 43.9$
		$cv = 16.0\%$		$cv = 7.1\%$		$cv = 43.9\%$
				$pe = 0.04$		$pe = 18.1$
Curly-tips (few curls)	8	*33.8*	*10.55*	*1.26*	*35.1*	*89.5*
		$sd = 3.9$		$sd = 0.07$		$sd = 31.8$
		$cv = 11.6\%$		$cv = 5.3\%$		$cv = 35.5\%$
				$pe = 0.02$		$pe = 12.0$
Long histerotrichs	10	*25.8*	*11.52*	*1.22*	*35.5*	*118*
		$sd = 4.7$		$sd = 0.08$		$sd = 47.1$
		$cv = 18.1\%$		$cv = 6.4\%$		$cv = 39.9\%$
				$pe = 0.03$		$pe = 21.0$
Medium histerotrichs	6	*20.1*	*10.31*	*1.20*	*36.4*	*177*
		$sd = 1.4$		$sd = 0.05$		$sd = 40.4$
		$cv = 7.2\%$		$cv = 4.3\%$		$cv = 22.8\%$
				$pe = 0.03$		$pe = 19.0$
Short histerotrichs	7	*19.5*	*9.68*	*1.19*	*36.0*	*170*
		$sd = 0.5$		$sd = 0.11$		$sd = 25.0$
		$cv = 2.4\%$		$cv = 9.4\%$		$cv = 14.7\%$
				$pe = 0.05$		$pe = 18.0$
Romney 2						
Chalky sickles	15	*37.3*	*8.91*	*1.27*	*36.7*	*42.6*
		$sd = 3.0$		$sd = 0.03$		$sd = 14.0$
		$cv = 8.3\%$		$cv = 2.4\%$		$cv = 32.8$
				$pe = 0.01$		$pe = 4.0$
Fine sickles	6	*40.0*	*9.19*	*1.24*	*35.9*	*40.9*
		$sd = 1.7$		$sd = 0.10$		$sd = 20.5$
		$cv = 4.3\%$		$cv = 7.8\%$		$cv = 50.1\%$
				$pe = 0.06$		$pe = 10.3$
Finer sickles	8	*35.0*	*8.69*	*1.31*	*36.1*	*49.1*
		$sd = 2.7$		$sd = 0.09$		$sd = 22.7$
		$cv = 7.7\%$		$cv = 7.0\%$		$cv = 46.2\%$
				$pe = 0.04$		$pe = 9.3$
Peak curly-tips (I)	10	*41.8*	*10.35*	*1.18*	*37.1*	*43.1*
		$sd = 4.1$		$sd = 0.07$		$sd = 9.3$
		$cv = 9.7\%$		$cv = 5.7\%$		$cv = 21.7\%$
				$pe = 0.04$		$pe = 3.1$
Curly-tips (II)	11	*41.5*	*10.64*	*1.23*	*37.1*	*50.8*
		$sd = 2.5$		$sd = 0.08$		$sd = 18.3$
		$cv = 6.1\%$		$cv = 6.4\%$		$cv = 36.0\%$
				$pe = 0.03$		$pe = 5.8$
Curly-tips (III)	11	*36.6*	*8.76*	*1.23*	*37.0*	*51.7*
		$sd = 2.0$		$sd = 0.05$		$sd = 16.6$
		$cv = 5.4\%$		$cv = 4.3\%$		$cv = 32.0\%$
				$pe = 0.02$		$pe = 6.3$
Curly-tips (IV)	12	*33.1*	*9.47*	*1.28*	*37.1*	*58.6*
		$sd = 2.5$		$sd = 0.08$		$sd = 27.3$
		$cv = 7.4\%$		$cv = 6.0\%$		$cv = 46.5\%$
				$pe = 0.03$		$pe = 9.1$
Long histerotrichs	16	*31.7*	*9.92*	*1.22*	*37.7*	*70.8*
		$sd = 1.7$		$sd = 0.10$		$sd = 23.6$
		$cv = 5.3\%$		$cv = 8.2\%$		$cv = 33.4\%$
				$pe = 0.03$		$pe = 6.3$
Short histerotrichs	11	*26.8*	*10.41*	*1.29*	*37.8*	*82.0*
		$sd = 3.2$		$sd = 0.05$		$sd = 18.5$
		$cv = 11.9\%$		$cv = 3.9\%$		$cv = 22.6\%$
				$pe = 0.02$		$pe = 6.6$

between the sickles and super-sickles of sample 770 ($P = 0.08$). Taking the results a whole, however, it seems safe to conclude that the later the follicles develop, the higher the plasticity of the fibers.

Reference has already been made to the fact that the ratio of primary to secondary follicles is very much higher for crossbred than for merino wools. Crossbred wools must, therefore, contain a much higher proportion of fibers of low plasticity, with the result that relaxation will proceed much more slowly than with merino wools during the storage of tops, yarns, and pieces during the manufacture of fabrics. This may well be the reason why the process of "crabbing" is so much more necessary with cross-

TABLE VI. AUSTRALIAN MERINO LAMB'S WOOL

Type of fiber	No. of fibers examined	Diameter (μ)	C.V. (%)	W (g. cm.$^{-2}$ $\times 10^5$)	E_1 (%)	k ($\times 10^{-5}$)
Sickles	10	*22.8*	*8.60*	*1.10*	*41.6*	*69.3*
		$sd = 4.0$ $cv = 17.5\%$		$sd = 0.07$ $cv = 6.2\%$ $pe = 0.02$		$sd = 8.8$ $cv = 12.7\%$ $pe = 3.3$
Early curly-tips	12	*25.2*	*8.69*	*1.03*	*42.6*	*92.0*
		$sd = 2.3$ $cv = 9.0\%$		$sd = 0.08$ $cv = 7.5\%$ $pe = 0.02$		$sd = 18.7$ $cv = 20.3\%$ $pe = 6.6$
Histero-trichs	9	*21.9*	*9.15*	*0.99*	*45.3*	*157*
		$sd = 1.5$ $cv = 6.9\%$		$sd = 0.10$ $cv = 9.8\%$ $pe = 0.03$		$sd = 85.4$ $cv = 54.4\%$ $pe = 32.3$

TABLE VII

Wool	Work required (g. cm.$^{-2}$ $\times 10^5$) for 30% extension of: Sickles	Early curly-tips	Late curly-tips	Long histero-trichs	Short histero-trichs
Lincoln 770	1.43	1.37	1.27	1.27	1.11
Lincoln 640	1.30	1.37	1.25	1.25	1.11
Lincoln 752	1.41	1.36	1.30	1.23	1.13
Lincoln 772	1.38	1.27	1.27	1.34	1.18
Lincoln lamb	1.32	1.09	1.09	1.16	1.03
Romney 1	1.42	1.23	1.26	1.22	1.19
Romney 2	1.28	1.18	1.23	1.22	1.29
Australian merino lamb	1.10	1.03	—	0.99	—

bred than with merino pieces. It is clear that the differences of plasticity revealed by this investigation have considerable practical importance, both for the wool grower and the manufacturer.

As regards the cause of the differences in plasticity, several possibilities can be eliminated at once. In the first place, they are not due to differences in the irregularity of cross-sectional area of different types of fiber, because there is no relationship between the values of k and the coefficients of variation in diameter. Secondly, the differences are not due to differences in the external conditions (climate and nutrition) under which the various types of fiber were grown, because the determinations of plasticity were made on the root ends of all fibers; although the growth rates of the different types of fiber are not identical, they are sufficiently similar to ensure that the lengths used grew at approximately the same time. Finally, the possibility that the differences in plasticity may be a specific property of the surface scale structure, since the latter is known to develop fissures at high extensions but well before the fiber breaks, can be rejected because the values of k for descaled fibers are so similar to those for normal fibers (Table II). The differences in plasticity must, therefore, be refered to differences in composition and molecular structure of the fibers as a whole. The nature of these differences will be discussed in a later paper.

Summary

A relationship between the order of development of the follicles in the skin of the sheep and the plasticity of the fibers to which they give rise has been established in the case of New Zealand Lincoln, New Zealand Romney, and Australian merino wools. Making use of Dry's scheme, in which chief attention is paid to the shape of the tips of the fibers, single staples, or a few staples from a small area of skin, were sorted into fibers of different types, which were classified according to the order of development of the follicles. The plasticity of the fibers was then measured by determining their rate of extension under constant load in water at 22.2°C. Primary follicles were found to produce fibers of lower plasticity than those of secondary follicles, and the order of plasticity of fibers of different types is, in general, the inverse of the order of development of the follicles.

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Some Fundamental Questions Concerning the Static Electrification of Textile Yarns: Part I*

V. E. Gonsalves

Research Laboratory, A.K.U. and Affiliated Companies, Arnhem, Holland

Introduction

It is peculiar that the explanation of the phenomenon of frictional electricity, which was known for a long time and which was the first phenomenon pointing to the existence of electricity (the more spectacular phenomenon of lightning is not considered for the moment), is still very insufficient. In a recent article, Harper [6] gave only a suggestion to explain the occurrence of frictional electricity between an insulator and a metal.

That frictional electricity is caused by the occurrence of a contact potential was (according to Perucca [15]) presumed by Volta; Helmholz [9], however, was the first to realize that frictional electricity—when two bodies are still in contact with each other—must be present as a double layer and that this double layer must be the seat of the contact potential.

The first theory about the origin of frictional electricity was given by Frenkel [4]; this theory is still fairly incomplete but is based on a reliable physical basis. Frenkel used the concept "intrinsic potential" in his theory, which is identical to the quantity presently designated as "work function of an electron" (the so-called "Richardson's φ"). He said that the electrons are "driven" from the material (*I*) with the smallest φ to the material (*II*) with the largest φ; than the material *I* becomes positive and the material *II* negative. How and why this takes place he could not explain by means of the scientific knowledge at that time. However, his view that frictional electricity is nothing but a passing of electrons from one material to the other is important.

In general, it can be said that this view is still accepted. However, some physicists are of the opinion that in the case of strong friction between the surfaces of the materials, not only the mechanism mentioned above but also other mechanisms of charge transition could occur.

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However, in the present study we shall confine ourselves to the case of little or no friction: in this case it is assumed that only electron transition from one surface to the other takes place.

Frenkel further considered the Helmholz double layer between the two touching surfaces to be a "condenser" with very large capacity. The distance p between the "plates" of the "condenser" would be very small (Figure 1), in consequence of which the capacity C of the system would be very large according to the formula

$$C = \frac{\epsilon O}{4\pi p}, \tag{1}$$

where O = surface of contact of the two substances and ϵ = dielectric constant.

The capacity C from formula (1) decreases considerably when the two surfaces are separated, as a result of which the potential increases enormously according to the formula

$$E = C^* V^*, \tag{2}$$

where E = the total surface charge of one of the substances (see Figure 1), C^* = the capacity of this material, and V^* = the potential of the same material.

In the original situation (where material *I* is pressed against material *II* and the capacity of the "condenser" is C),

$$E = CV, \tag{3}$$

where V, according to Frenkel, is of the order of the contact potential, and hence of the order of 1 volt.

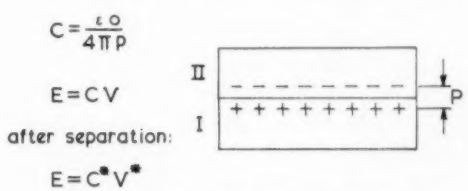


FIG. 1. *Helmholz' "condenser."*

According to the results of Heiszner's investigation [8], this estimation of V is on the high side. On the basis of his measurements on the maximum static electrification he calculated V (for $p = 10$ Å.) and found it to be of the order of 0.03 volt. (In 1879 Helmholz [9] also estimated the distance p of his double layer to be approximately 10 Å.)

Assuming the estimation of the distance p to be correct, it follows, according to Frenkel that a field intensity of the order of 10^7 volt/cm. would prevail in the "condenser"; but at such a high field intensity, ionization (and disruptive discharge) of the air, which must still be present between the contact surfaces, will certainly occur. In the present author's opinion, this ionization—which makes a further increase of the surface charge impossible—is the reason why Heiszner found only about 0.03 volt for V; thus, the field intensity actually occurring in the "condenser" in friction experiments is about $100\times$ as small (about 10^5 volt/cm.); this can, indeed, be considered a reasonable maximum value, at which ionization just does not occur, when it is taken into account that the estimation of p is somewhat on the low side.

It has been observed by many investigators that in experiments on static electrification there is a maximum charge which cannot be exceeded.

One reason for the occurrence of maximum charge is the air ionization, as noted above. A short time ago this was further studied by Medley [13]. He found that the maximum attainable static electrification could be increased by 50% to 100% if the friction experiments were carried out in (dry) air saturated with carbon tetrachloride rather than in (dry) air (the fact is that carbon tetrachloride has a considerably higher dielectric strength than air).

A second reason for the occurrence of maximum charge is the "leakage" which always occurs to a greater or lesser extent at the "condenser." The electrons passed from one material to the other tend to leak back because of a certain extent of conductivity of the dielectric of the "condenser." Besides, due to the nature of the two friction surfaces, this leakage is determined by the state of humidity of the surfaces; this is the reason why frictional electricity can never be generated with moist surfaces. It *is* possible to generate frictional electricity in an atmosphere of relatively moist air by rubbing two well-dried surfaces against each other. However, the phenomenon decreases soon because the surfaces are gradually covered with a moisture layer. Therefore, in a somewhat moist atmosphere the maximum value of the electrostatic charge occurs because of an equilibrium being reached; on continuous rubbing, as many electrons pass from material *I* to material *II* as "leak back" from material *II* to material *I*. Therefore, this maximum charge is smaller than when the experiment is made in a dry air atmosphere.

When one or two of the materials are hygroscopic, the leakage phenomenon plays a very important part; this is the reason why the static electrification decreases with increasing relative humidity of the air when, for example, rayon is rubbed against metal.

Ultimately we shall have to examine the phenomenon of the static electrification of textile yarns, which pass over thread guides of metal (or of other types of material), and the problem of opposing this phenomenon.

When reading the publications on this subject—*i.e.*, of Keggin, Morris, and Yuill [10], Gerard [5], Hayek and Chromey [7], Neuhof [14], Taylor [18], Lehmicke [12], Medley [13], and Harper [6]—it is striking how seldom a theoretical picture is used for the interpretation of the results observed. The reason is clear: there does not exist a clean-cut theory which explains the phenomenon of static electrification. Yet the availability of such a theory—even as a "working hypothesis" only—is of great importance to further experimental investigations. It is for this reason that we shall try herein to widen our knowledge of the phenomenon of static electrification.

Before discussing the theory we will pose fundamental questions which establish the problems connected with the phenomenon of static electrification.

(*1*) When two substances of different materials are rubbed against each other, electrons of one substance pass to the other. Why don't the electrons pass back in consequence of the potential difference formed in the double layer?

(*2*) When the maximum charge has not yet been reached, there is a potential difference in the double layer. Why, on continued rubbing, do electrons pass from one material to the other "against this potential difference"?

(*3*) An "electrostatic series" of various materials can be drawn up, in which a material listed above (or before) another is positive with respect to this other material. Why is it that the electrostatic charge between a material at the beginning and one at the end of the series is not much larger than the charge between two successive materials?

(*4*) The only known (empirical) interrelationship in the field of the phenomenon of static electrification is Coehn's rule [3]: when two insulators are rubbed against each other, the insulator with the highest dielectric constant will become positive. Can this be understood from the theoretical point of view?

(*5*) When two equal materials are rubbed against each other—*e.g.*, polystyrene against polystyrene—a $+(-)$ or a $-(+)$ charge is generated, although this charge is slight. Can this be explained theoretically? A difference in surface finishing—*e.g.*, rough polystyrene rubbed against smooth polystyrene—gives: $p_r +$, $p_s -$. How can this be explained?

(*6*) When rubbing equal materials with different densities against each other, the material with the largest density becomes + (Hesehus-Georgiewski [2]. How can this be explained?

After discussing the theory, we shall return to this questionnaire.

The Theory of the Phenomenon of Static Electrification

Section 1

For the present discussion we shall confine ourselves to one case—*viz.*, the rubbing of an insulator against a metal (system *I-M*).

As already mentioned, we consider the passing of electrons from *M* to *I* or vice versa as the cause of static electrification. A lack of electrons means that the material becomes positive; an excess of electrons means that it becomes negative.

First we will discuss the present-day conceptions of the properties of a metal (and an insulator) in connection with the energy states of an electron which is present inside or outside the metal (or the insulator).

A block of metal is shown schematically in Figure 2. When an electron, coming from infinity, passes through the block of metal along the dashed line, the potential energy of the electron changes according to the (thick) drawn line in Figure 3; thus, the potential energy of the electron is less inside than it is outside the block. However, an electron can move freely in the metal; in this case the total energy ($E_{pot} + E_{kin}$) of this electron is represented by a horizontal line higher than the E^*_{pot} level. Since very many energy states are possible in the metal, the states of motion of the electrons in the metal are represented in Figure 3 by a number of these horizonal lines. All of the "energy levels" indicated in Figure 3 are occupied by electrons; according to Pauli's principle, only two electrons can be present on each energy level (these electrons then have a mutually opposite spin). Over the "occupied" energy levels given in Figure 3 there are many "unoccupied" energy levels, which have not been indicated in the figure.

When a kinetic energy equal to $e\cdot\varphi$ *e*-volt * is added to an electron present on the highest (occupied) energy level, this electron can leave the metal. This φ is a constant which is characteristic of any metal and is called "Richardson's φ." For various metals φ amounts to about 1 to 5 volts (p. 193 of [19]).

What shape has the energy scheme for an insulator? This is shown schematically and as simply as possible in Figure 4. We distinguish here bands of energy levels, separated by regions of energy states, in which an electron cannot be present.

The bands *1* and *2* in Figure 4 are "fully" occupied; this means that all the energy levels are occupied and therefore the electrons present on them cannot participate in conduction (in order for an electron to participate in conduction, it must obtain extra kinetic energy and must be on a higher energy level; since all the higher energy levels in the band are already occupied, the electron cannot obtain this extra energy).

The band *3* is "empty"; no electrons are present here, which could give conductivity to the substance.

Increasing the temperature may cause electrons to jump from band *2* to band *3*; then the "insulator" becomes somewhat conductive. Whether this happens or not—at not too high an increase in temperature—depends on the potential difference ΔE between band *2* and band *3*: when $\Delta E > 0.5e$-volt, the substance is called a "good insulator;" when $\Delta E < 0.5e$-volt, it is

* An *e*-volt is equal to that kinetic energy which an electron obtains when passing through a potential difference of 1 volt (e = charge of an electron).

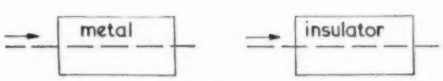


FIG. 2

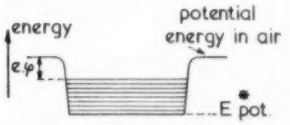


FIG. 3

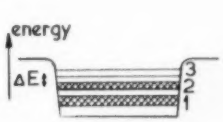


FIG. 4

called a "semiconductor." Thus, the electric conductivity of semiconductors increases with increasing temperature (p. 194 of [19]).

The above conceptions of the properties of metals and insulators, as schematically shown in Figures 3 and 4, have been known for almost 20 years. With the aid of these conceptions, how is the phenomenon of static electrification to be explained? Without a deeper theoretical insight this appears to be rather difficult, if not impossible; we will study only one of the difficulties more closely.

If, in the case of contact between a metal and an insulator, electrons pass from the metal to the insulator, according to the above they can only find a place in the free energy bands. In these bands the electrons can, in general, move freely; this means that the insulator should become somewhat conductive. This would mean that a negatively charged insulator could be discharged easily—*viz.*, by connecting the insulator at one point of its surface to the earth. Experiment shows that this certainly is not the case: the spot of the insulator surface which is connected to the earth can, indeed, discharge, but the remaining surface persistently retains the electrostatic charge; this means that after being charged the insulator still remains an "insulator."

It is this difficulty in particular which makes us realize that, strictly speaking, we shall never be able to explain the phenomenon of static electrification by means of the present conception of an insulator.

In section 2 we shall widen these conceptions somewhat, and in the sections following we shall show that with the aid of the new conceptions a great number of hitherto unexplained phenomena of static electrification can be explained in a rather simple way.

Section 2

Since no direct explanation can be given of the occurrence of the phenomenon of static electrification by means of the conception of an insulator shown in Figure 4, it will be necessary to assume, by way of hypothesis, the existence of more energy states of the electrons.

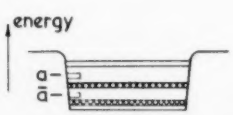


FIG. 5. *Situation before (negative) charge of the insulator.*

Let us first consider the case when the insulator is charged negatively: obviously, electrons can adhere to the surface of the insulator, which is connected with loss of energy. Moreover, these electrons will not be allowed to participate in conduction (in the charged condition the insulator still remains an insulator); in other words, the electrons may have some freedom of movement, but this freedom must be limited. These two conditions are shown schematically in the energy diagram of Figure 5; the rectangle means that a charging electron taken up will possess only a limited freedom of movement; the place of the rectangle in the diagram indicates how large $E_{kin} + E_{pot}$ of the charging electron taken up will be. Figure 5 shows only two possibilities: at a the charging electron taken up will adhere less strongly to the insulator surface than at $\bar{a}$.

Let us now consider the case when the insulator obtains a positive charge: on the surface of the insulator electrons must be present, which, under suitable circumstances, can detach themselves; such electrons leave "holes" behind, which must be regarded as positive charges $(+e)$. Here, too, it must be assumed that it is not possible for the "holes" to participate in conduction (for this type of conductivity see Kendall [11]). Both conditions are given in the rectangles a' and $\bar{a}'$ in Figure 6. In general, these rectangles will lie on different energy levels than the rectangles a and $\bar{a}$ in Figure 5. (The cross in Figure 6 indicates that the "hole" in question is still provided with an electron: situation before charging the insulator.)

Since a positive as well as a negative charge can be imparted to an insulator, the energy diagram will have to be a combination of the diagrams drawn in Figures 5 and 6. In connection with the following and for clearness, the two types of diagrams will for the present be kept separate.

The concept of electron surface energy levels is not new. In 1932 these surface energy levels were proposed on theoretical grounds by Tamm [17]; they play an important part in the present-day investigation of semiconductors (Shockley and Pearson [16]).

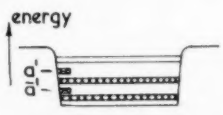


FIG. 6. *Situation before (positive) charge of the insulator.*

In his calculations Tamm considered only the case of a material with a crystal structure; in the present author's opinion, however, every material whose structure shows a certain periodicity must possess these surface energy levels.

What happens when a metal and an insulator approach each other? First of all, we examine the line of the potential energy of an electron, passing through the two materials at various distances between the materials (see Figure 7).

In Figure 7(a) the distance between the two materials is still large; an electron present on the dashed line between M and I will possess a potential energy equal to the potential energy at an infinitely large distance from the substances, $(E_p)_\infty$.

In Figure 7(b) M and I have approached each other to a distance of the order of 10Å. (range of Thompson's mirror-image force, p. 219 of [19]). In this case an electron between M and I will feel the presence of the metal as well as of the insulator; thus, the top, T, of the potential barrier will be lower than $(E_p)_\infty$.

In Figure 7(c) the distance between M and I is minimum; in this case T will be even lower. The shorter the average distance between M and I caused by the stronger rubbing between the metal and the insulator, the lower the potential barrier.

Let us now combine, for this case of close contact, the diagram of Figure 3 with the diagrams of Figures 5 and 6 (see Figure 8).

In Figure 8(a) the potential barrier has fallen so far that a metal electron can enter the a space without addition of extra energy. The now free energy level ϵ in the metal is immediately occupied by an electron which was present on a higher energy level, in consequence of which the return of the charging electron in a is blocked; thus, the metal becomes + and the insulator −.

In Figure 8(b) the potential barrier has fallen so far that an electron from an a' space can reach the energy level ϵ' in the metal without addition of extra energy. Once the electron is present on this energy level, it will immediately fall back on the lowest unoccupied energy level in the metal (all this is in agreement with the Fermi-Dirac statistics as regards the occupation of the available energy levels); the electron has then lost energy and cannot (without addition of energy) return via the potential barrier to the a' space. In the latter case, the metal becomes − and the insulator +.

The above illustration explains not only why the electrons pass from one substance to the other, but also why their return is blocked.

Let us consider again the situation of Figure 8(a): after the charging process there are charging electrons in the a spaces on the surface of the insulator. Immediately opposite the a space a small zone is formed in the metal in which the electron density is lower than in other places in the metal, because the electrons which enter this zone are repelled by the charging electron in the a space of the insulator (this can also be expressed as follows: the stay of the electrons in

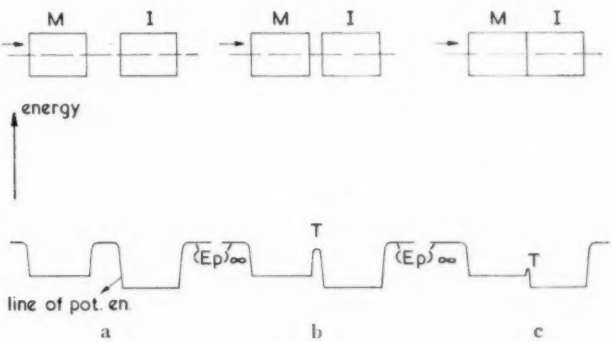


FIG. 7

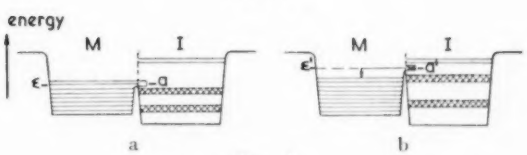


FIG. 8

the zone in question is shorter than in a similar zone somewhere else in the metal). This zone with its lower average electron density finds expression as a positive charge (lack of electrons). Therefore, opposite to all charging electrons on the surface of the insulator are formed positively charged zones on the surface of the metal. In this way Helmholz's double layer appears unconstrainedly.

The situation of Figure 8(b) can be considered in the same way: after charging, electrons leave the insulator surface, thus forming positive a' holes. Immediately opposite the a' hole a zone is formed in the metal in which the electron density is higher than elsewhere in the metal; such a zone is charged negatively (a surplus of electrons). Thus, all these negatively charged zones and the corresponding positive a' holes again form Helmholz's double layer.

Section 3

Let us now consider the particular case of an "activated" insulator which is rubbed against a metal. What is meant by an "activated" insulator?

It has already been noted that on the surface of an insulator there must be places which can take up an electron (a spaces) and also places which can deliver an electron (a' spaces). Let us assume that the situation is as indicated in Figure 9: the electrons which (before charging) are present in the a' spaces adhere less firmly to the insulator surface than the electrons which (after charging) are present in the a spaces.

The special feature of this case is that this energy state of the insulator does not seem probable, because the electrons on the insulator surface always occupy the places with the lowest energy states. However, this case could to some degree be compared with the metastable states which can occur in activated atoms. In this case we will call the insulator an "activated" insulator.

Figure 9(a) shows the situation for the case of relatively low normal pressure; the potential barrier has fallen so far that the metal will obtain a negative and the insulator a positive charge. Figure 9(b) shows the situation for the case of high normal pressure; the potential barrier has fallen so far that metal electrons can also pass to the insulator; if there are more electrons passing in the latter case than in the former, the metal obtains a positive and the insulator a negative charge.

Thus, when an insulator is rubbed against a metal, at low normal pressure the metal *can* become − and the insulator +; at higher normal pressure the metal *can* become + and the insulator −. In Part II of this series it is shown that, indeed, this "reversal of sign" of the charge, which is dependent on the normal pressure, often occurs in practice.

Is it also possible that the reverse occurs—*viz.*, that at low normal pressure the metal first becomes + (insulator −) and at higher normal pressure the metal becomes − (and the insulator +)?

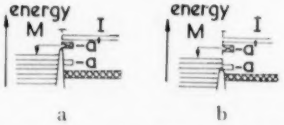
Figure 10 shows the situation in which for low normal pressure the metal becomes + (and the insulator −); however, it also appears from the figure that at higher normal pressure (potential barrier is indicated by the dashed line) the total passage of electrons continues to occur in one direction; in other words, when a metal against which an insulator is rubbed becomes *positive* at low normal pressure, according to our considerations *the sign of the charge cannot change* by increasing the normal pressure.

Anticipating the experimental results, which will be described in Part II of this series, it can now be stated that this type of charging (metal first + and at higher normal pressure −) has not been found in our experiments carried out up to now.

Section 4

Up to now it was assumed tacitly that the surfaces of the metal and the insulator were "flat"; this means that the unevenness is not greater than of the order of a few Å., for only in this case can it be said that the mutual distance of the surfaces is about 10 Å.

Actually, we are dealing with far greater surface unevenness; when an insulator is pressed on a metal (see Figure 11), the two substances will really contact on a certain number of surfaces Δ_0 only; the consequences is that static electrification does occur, but it will, in general, be small.



a b

FIG. 9. *Situation before charging.*

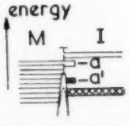


FIG. 10. *Situation before charging.*

The total surface of contact can, however, be increased by a larger normal pressure and in particular by rubbing, as a result of which, according to the theory, the static charges increase; experience shows that this is indeed the case. We emphasize that, strictly speaking, the not-too-hard rubbing of the surfaces against each other only serves to effect a closer contact between the surfaces, as a result of which higher charges occur; however, in principle it is the contact itself which gives rise to the occurrence of the charges (see also Neuholf [14]).

As regards the influence of temperature, the following can be stated: when the temperature of a metal is increased, higher energy levels will be occupied with electrons: In the case of an insulator, which obtains a positive charge when rubbed against metal at room temperature, it is less probable that electrons will pass from the insulator to the metal when the temperature of the metal is higher. Since, however, the Fermi-Dirac statistics regarding the occupation of energy levels in the metal change only a little at increases in temperature of about 100°–200°K, it must be expected that the above-mentioned effect will be small.

The Questionnaire

We now return to the questionnaire mentioned in the introduction on page 712. Strictly speaking, a few of these questions have already been answered by our theoretical considerations. We shall go more deeply into the other questions.

(*1*) The electrons passed from one substance to the other cannot pass back because they are blocked; the mechanism occurring is discussed thoroughly on page 715.

(*2*) The answer to this question is in the very small distance p (see Figure 1) of the double layer. Consider the passing of electrons from the insulator to the metal (Figure 12). According to our considerations, negative zones in the metal surface lie opposite to positive holes in the insulator surface; the distance p of the double layer would amount to about 10 Å.

A further passage of electrons is now only possible when the average distance l between the holes in the insulator surface is much larger than 10 Å.; then an electron e passing from one surface to the other will not be influenced at all by the presence of the neighboring dipoles. Therefore, according to the above, at maximum state of electrification $l \gg p$ must apply.

From experiments carried out in our laboratory and from the data of Heiszner [8], we have calculated this average distance l to be ~ 700Å. Thus, it appears that, for the maximum state of electrification, l is much larger than p.

(*3*) In the discussion of the theory we saw that an electron, without addition of energy, will pass from one material to the other whenever it gets the opportunity to do so. Thus, the magnitude of static electrification will depend primarily on the number of electrons which *can* pass. Whether the material against which another material is rubbed will become positive or negative depends only on the mutual position of the energy levels of the surface electrons. This consideration makes it understandable that the static electrification between two materials at the beginning and at the end of the electrostatic series need not be much larger than the electrification between two successive materials of the series.

(*4*) The insulator with the highest dielectric constant is most easily polarizable in an electric field; this means that for this material the electrons are not bound very tightly to the positive atomic nuclei. The surface electrons of this material will show a tendency to pass to the insulator with the lower dielectric constant; in general, the electron energy levels of the surface of the latter material will be lower than those of the surface of the former material.

(*5*) It has already been noted (see page 716) that an insulator surface can be activated; the surface electrons can be in very high (metastable) energy states. By rubbing such an activated surface against

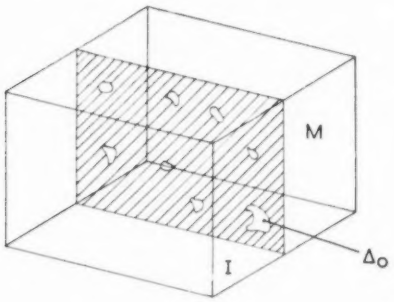


FIG. 11

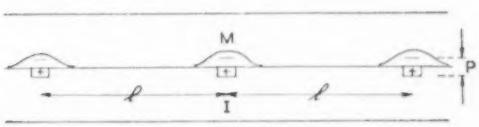


FIG. 12

a neutral surface of the same material, a positive charge will be imparted to the activated surface. Since it is expected that each insulator surface locally shows some activation, it is clear that on rubbing polystyrene against polystyrene, sometimes a $+(-)$ charge or a $-(+)$ charge is observed, and that this charge is slight.

When a polystyrene surface is roughened considerably, obviously the surface is activated strongly; consequently, on rubbing against a smooth polystyrene surface, p_r becomes $+$ and $p_s -$.

(*6*) The energy levels of an electron in a free atom are much lower than those in the crystal lattice; this is due to the presence of other atoms which, together with the first-considered atom, form the solid matter (Zwikker [19], p. 193). An increase in density of the solid matter will raise the energy levels of the electrons even more. Therefore, when two equal materials of different density are rubbed against each other, the material with the highest density will become positive.

Concluding Consideration

In this article theoretical considerations on the phenomenon of static electrification, in particular for the case metal-insulator, have been established. The theory provides answers to some hitherto unanswered questions. In any case, it will be possible to use the theory as a working hypothesis for further experimental investigations.

The next step was the development of a measuring apparatus, by means of which static charges on textile yarns can be measured. Both apparatus and measuring arrangement will be elaborately dealt with in Part II of this series. In Part II a few preliminary experimental results will be discussed as well. It will be seen that our theoretical considerations help in the interpretation of these experimental results.*

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* Shortly before this article went to press, a Conference on Static Electrification organized by the Institute of Physics was held in London (Mar. 25–27, 1953).

This conference, at which some twenty lecturers dealt with the most divergent aspects of static electrification, opened with an important speech by Prof. F. A. Vick (University College of North Staffordshire) on the theory of the phenomenon.

It may be stated here that the way in which Prof. Vick approached this problem was similar to that set forth above. All the papers presented at the Conference, including Prof. Vick's lecture, will be published soon as a supplement to the *British Journal of Applied Physics.*

Preparation of Soluble Yarns by the Carboxymethylation of Cotton

George C. Daul, Robert M. Reinhardt, and J. David Reid

Southern Regional Research Laboratory, New Orleans, Louisiana*

Abstract

Water- and alkali-soluble cotton fibers, yarns, and threads have been prepared by two methods. The cotton is preferably pretreated by pressure-kiering in 2% sodium hydroxide to remove the noncellulosic materials, and then treated with monochloroacetic acid and sodium hydroxide by either a one-step or a two-step process. Where only disintegration or partial solubility is required, the one-step method is sufficient. Where complete solubility of the cotton is required, the process must be carried out in two steps: a mild, followed by a stronger treatment. The treated cotton is neutralized in alcohol with acetic acid to produce water-soluble products or with strong acids in alcohol to produce water-insoluble but alkali-soluble products. Cotton in the form of sliver, yarn, and thread has been successfully treated.

THE PREPARATION of water- and alkali-soluble yarns by the partial carboxymethylation of cotton cellulose was briefly described in a letter to the Editor of TEXTILE RESEARCH JOURNAL [7], and a patent has been issued on the products [2]. Details are given here of the preparation of soluble fibers, yarns, and threads by two methods, and some of the properties of the resulting products are reported.

The process differs from that used in the commercial production of water-soluble sodium carboxymethylcellulose powder (for use in detergents, foods, etc.), in which wood cellulose is usually first treated with sodium hydroxide, and then with monochloroacetic acid, with beating and mixing. This procedure would be ineffective in producing a soluble yarn or thread from cotton cellulose since the sodium chloroacetate formed in the reaction is only slightly soluble in strong sodium hydroxide solution, and thus would not penetrate sufficiently into the fibers to give a uniform treatment. In the production of soluble yarns and threads, the cotton is purified by pressure-kiering in 2% sodium hydroxide solution or by boiling in monoethanolamine to remove noncellulosic materials. The purified cotton is soaked or padded with a solution of monochloroacetic acid, centrifuged to remove the excess liquid, and then treated with a strong solution of sodium hydroxide. By this procedure, the sodium chloroacetate is formed within the fibers; this results in a uniform treatment without apparent structural damage to the fibers.

It is possible to produce the carboxymethylated cotton fibers, yarns, and threads in a wide range of solubilities. The degree of solubility depends upon the amount of carboxymethyl substitution, which may be controlled within limitations.

The soluble cotton products have several advantages over the alkali-soluble alginate fibers [1]. They may be produced either in the free acid form, which is water-insoluble but alkali-soluble, or in the form of the sodium or ammonium salts, which are soluble in ordinary tap water. Any of these forms would have considerably more tensile strength than that attributed to the alginates.

Lace and embroidery makers, shirt manufacturers, upholsterers, fur blenders, and meat packers have shown interest in the soluble cotton products. Some of these potential users of soluble yarns and threads have indicated the need for a completely soluble fiber, while others have shown interest in a less soluble fiber which is capable of disintegration in water.

In general, these needs have been met by studies of the technology of the process. These studies, described below, involve experiments with the single and the two-step carboxymethylation methods, and include consideration of methods of pretreatment, the alcohol wash, and neutralization procedures.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Some properties of the products, such as spinnability, weaveability, and moisture regain, were investigated. A method of analysis of the degree of substitution suitable for use over the entire substitution range was devised.

Preparation of Soluble Cotton Products

Pretreatment

To determine the best method for removing the natural waxes of cotton and putting the cotton in the most reactive condition for carboxymethylation, the effects of the following seven pretreatments on 12/5 cotton sewing thread were compared: extraction with alcohol; extraction with acetone; boiling in 2% sodium hydroxide solution for 2 hrs.; mercerization with and without tension in 20% sodium hydroxide solution for 1 hr.; kiering under 15 lbs. pressure in 2% sodium hydroxide for 5 hrs.; boiling in monoethanolamine for 5 hrs. The four sodium hydroxide-treated skeins and the monoethanolamine-treated skein were washed in water and neutralized with a 5% solution of acetic acid, rewashed, and dried.

The samples treated as above and a control sample were soaked in 20% monochloroacetic acid solution, centrifuged to 50% retention, immersed in 50% sodium hydroxide solution for 1 hr., and then neutralized and washed in alcohol containing 5% acetic acid. Breaking strengths and elongations of the samples before and after carboxymethylation and the carboxymethyl substitutions are shown in Table I, and will be discussed later.

Single and Two-Step Treatments

Partially carboxymethylated cotton with a substitution of 1 carboxymethyl group per 7 or more anhydroglucose units is highly swellable and reactive, but is insoluble in water. The borderline of solubility is reached when there is a substitution of 1 carboxymethyl group per 4 to 6 anhydroglucose units. With this degree of substitution, the fibers become gelatinous, lose all their strength, and disintegrate in water, but do not completely disappear. A product in this borderline range of solubility may be obtained by a single treatment with strong monochloroacetic acid solution and concentrated aqueous sodium hydroxide. Carboxymethylated cotton in the soluble range has a substitution of 1 carboxymethyl group per 1 to 3 anhydroglucose units.

Maximum solubility may be obtained by two carboxymethylations of purified cotton. The two-step process takes advantage of the insoluble range of partially carboxymethylated cotton. The cotton is first treated with a relatively mild concentration of monochloroacetic acid and strong sodium hydroxide solution to effect a substitution of about 1 carboxymethyl group per 10 to 15 anhydroglucose units. The cotton thus modified is highly swellable and reactive. It is then treated with strong monochloroacetic acid and strong sodium hydroxide solution. On removing the residual alkali with acid in alcohol or other water-miscible organic solvent, a product is obtained, completely soluble in water, in which the fibrous nature of the cotton is retained.

TABLE I. EFFECT OF PRETREATMENT ON PARTIAL CARBOXYMETHYLATION

Pretreatment	Breaking strength (lbs.)	Elongation (%)	Carboxymethylated breaking strength (lbs.)	Carboxymethylated elongation (%)	Carboxymethyl substitution (Carboxymethyl group: anhydroglucose units)
None (control)	9.8	12.9	8.7	25.1	1:11
Acetone-extracted	10.8	12.4	8.6	29.4	1:8
Alcohol-extracted	11.3	13.1	9.0	26.3	1:8
2% Sodium hydroxide-boiled	8.7	13.9	8.2	25.8	1:8
20% Sodium hydroxide, loose-mercerized	9.6	31.2	8.8	32.2	1:8
20% Sodium hydroxide, tension-mercerized*	9.7	12.7	9.4	20.8	1:9
Pressure-kiered in 2% sodium hydroxide	8.2	15.4	7.7	35.3	1:6
Monoethanolamine-boiled	9.2	16.1	7.9	33.4	1:7

* Skein held at constant length during mercerization.

Treatment of Cotton Sliver

A possible use for soluble cotton is in blending with other fibers before spinning; therefore, cotton in the form of sliver was carboxymethylated by the two-step process.

One pound of card sliver made from Delfos cotton was pretreated by extraction with hot alcohol in a Soxhlet apparatus. It was then divided into three equal parts, and each part was wound into a skein. One part was left untreated. A control sample was prewet with water containing a wetting agent, centrifuged to about 50% pickup, soaked in 50% sodium hydroxide solution for 1 hr., centrifuged again, neutralized with 5% acetic acid in alcohol, washed with 95% alcohol, and dried. The remaining portion was first carboxymethylated by soaking in a 20% solution of monochloroacetic acid containing a wetting agent, centrifuged, treated with 50% sodium hydroxide solution, centrifuged, neutralized and washed in alcohol as in the control sample, and dried. This sample was re-treated first with 50% monochloroacetic acid and then with 50% sodium hydroxide solution using the same technique as before to give a soluble product.

These samples were processed into yarns by a procedure to be described in a later section.

Treatment of Yarns and Threads

Yarns and threads were carboxymethylated by either the single or the two-step treatment, depending on the degree of substitution (degree of solubility) desired. The single treatment consisted of impregnating pretreated yarns or threads with a 50% solution of monochloroacetic acid, centrifuging to about 60% pickup, and then soaking in 8 parts by weight of 50% sodium hydroxide solution. With this proportion of reagents the temperature rose to about 45° to 50°C. (Too much alkali gives a product with poor solubility while too little results in localized overheating, which tends to gelatinize the cotton.) The treated cotton was then centrifuged, washed, and neutralized with acetic acid in alcohol.

To obtain products of greater solubility the two-step treatment was used. The pretreated yarn or thread was first impregnated with 15% monochloroacetic acid solution containing a wetting agent, centrifuged, and treated with 50% sodium hydroxide solution for about 20 min., then neutralized with acetic acid in alcohol, washed in alcohol, and dried. The products of this treatment had a substitution of about 1 carboxymethyl group per 10 to 12 anhydroglucose units. Products in this range of substitution were discussed in more detail in another publication [3]. The modified cotton was then treated successively with 50% monochloroacetic acid and 50% sodium hydroxide solution. It had a substitution of 1 carboxymethyl group per 2.5 anhydroglucose units. Breaking strength was about 95% of that of the original yarn or thread.

Treatment of Thread on Semi-Pilot-Plant Skein Mercerizing Equipment

A 1-lb. batch of soluble thread was prepared on a semi-pilot scale frame-type mercerizer [4] by the two-step carboxymethylation treatment under conditions which approximated commercial processing.

One pound of 7/2 mercerized cotton thread was made into a loosely leashed skein, and this was treated in 15% monochloroacetic acid. It was centrifuged to about 65% wet pickup and then placed on the mercerizer and rotated through a 50% solution of sodium hydroxide, allowing some initial shrinkage to obtain good penetration. After about 10 min., the skein was rotated through a 5% solution of acetic acid in alcohol, and then through alcohol alone. When neutralized, the thread relaxed and could be stretched to its original length. After drying the skein, the process was repeated, except that 50% monochloroacetic acid followed by 50% sodium hydroxide was used.

In commercial practice, the alcohol could be recovered as well as the salts formed in the reaction. Salts could be kept to a minimum with careful processing control, and the strong caustic solutions used in the process could be reused a number of times with occasional fortification.

Processing Problems

In the suggested applications for soluble fibers, yarns, and threads, mill processing is a very important factor. To ascertain if there were any special problems involved in the processing of carboxymethylated cotton, soluble products were spun and woven.

Untreated and mercerized sliver and the sliver that had been carboxymethylated in the experiment described above were passed through the rolls of a laboratory padder to flatten and separate the individual strands, and then passed through a drawing

frame. The untreated cotton went through the drawing frame without difficulty. However, both the mercerized and the soluble sliver had high friction characteristics which made the drawing operation difficult. Lubrication with a light machine oil in acetone overcame this difficulty. Other lubricants and softeners which were effective were Turkey red oil, Triton K-60,* sorbitol, Onyxsan 200,* and Onyxsan H,* used in 1% solution in either acetone or alcohol. It was also noted that Aerosol OT * was an effective softening agent. After drawing, the sliver samples were spun into roving and then into 30's yarn without difficulty.

To test the feasibility of weaving soluble cotton and removing it after weaving, a 2-ply, 16's yarn was carboxymethylated to the soluble state and woven as filling in a plain cotton warp, alternating every other inch with plain cotton filling. A part of the fabric thus obtained was washed in running tap water and passed through squeeze rolls several times between washings. The soluble yarns disintegrated, leaving spaces where they had been, except where they were tightly woven, as in the selvage. In tightly woven yarns the fibers cannot swell sufficiently to disintegrate and go into solution. Hence, looseness of twist or weave is important in the use of soluble cotton. Carboxymethylated cotton, being a high polymer, characteristically becomes gelatinous before going into solution. Passing the fabric through rolls aids in rupturing the primary walls of the cotton and greatly accelerates the disintegration. The use of soap to wash out the last traces of fiber should be avoided because soap tends to insolubilize the material. Detergents which do not react with the carboxymethyl group may be used.

Analytical Procedure

Because of the water-solubility of the carboxymethylated cotton samples produced in these experiments, it was difficult to completely remove by-product salts which would interfere with ordinary analysis for the carboxyl group. The method formerly used [6] gave inconsistent results. This method consisted essentially of converting the partially carboxymethylated cellulose to the copper salt and analyzing for copper content. Complete removal of such substances as sodium acetate, sodium chloride, and sodium carbonate by alcohol washing was impractical.

The difficulties were overcome by soaking the water-soluble samples in 80% ethyl alcohol containing 2% hydrochloric acid for about 3 hrs. to convert them to the free acid form of carboxymethylcellulose. This product is insoluble in water, so that water can be used to wash out the by-product salts. After the samples are dried and weighed, they are placed in flasks and covered with water to which an excess of standard 0.1*N* sodium hydroxide is added. The flasks are stoppered and allowed to stand for a minimum of 3 hrs., but preferably overnight, and are then back-titrated with standard hydrochloric acid, using phenolphthalein as an indicator.

Effects of the Variables of the Treatment on Properties of Products

Effects of Pretreatment

From Table I it is apparent that a higher degree of substitution was obtained in all of the pretreated samples than in the control. However, as will be shown later, the kier-boiled and monoethanolamine-treated samples when carboxymethylated gave the most soluble products.

Effect of Concentration of Alcohol Wash

In the first attempts to prepare soluble cotton threads, the samples were washed with various concentrations of alcohol ranging from 60% to 95%. It was observed that when the lower concentrations were used, the treated samples were stiff, had increased in thickness, and had lost much breaking strength. However, when 95% alcohol was used, samples were soft and retained almost all of their original breaking strength. A study under the microscope of water-soluble cotton offered a possible explanation for the stiffness, strength loss, and increase in thickness in samples washed with the dilute alcohol.

Figures 1 to 6 show views of a longitudinal section of a single water-soluble cotton fiber prepared from mercerized cotton thread mounted in alcohol solutions of 95%, 60%, and 50% concentrations. The photomicrographs show that no swelling occurs in the fiber mounted in 95% alcohol and noticeable swelling occurs in the 60% alcohol. With 50% alcohol, uniform swelling occurred at first, followed by the ballooning phenomenon usually seen when

* The mention of trade products does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

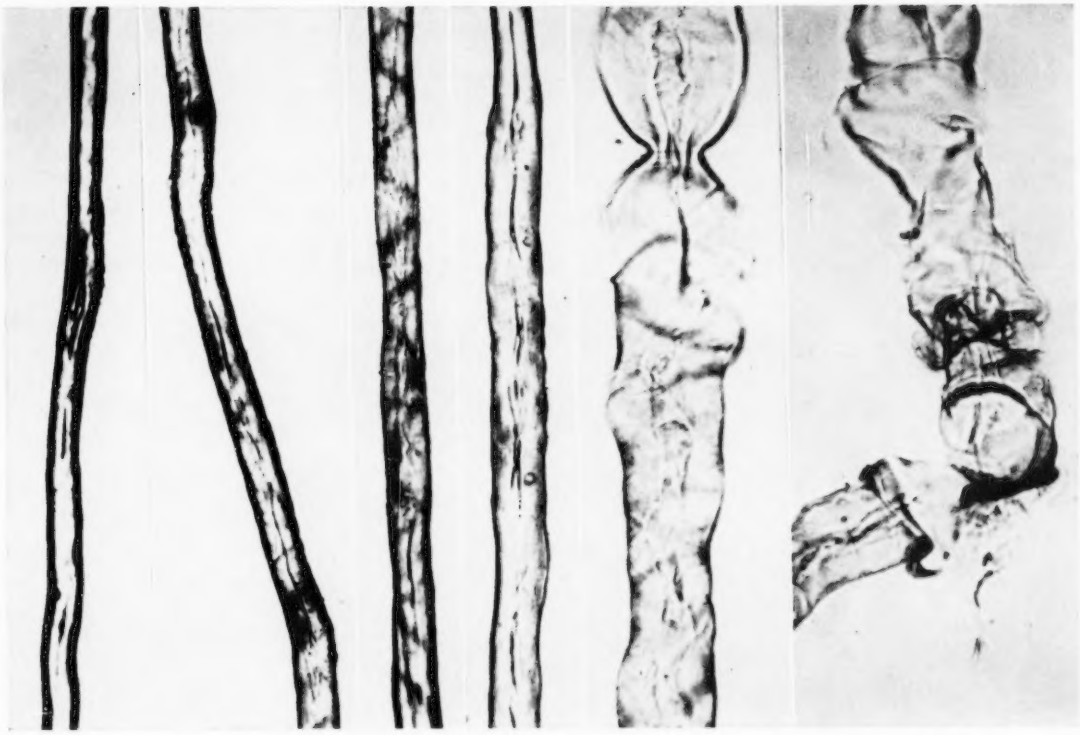

Fig. 1 Fig. 2 Fig. 3 Fig. 4 Fig. 5 Fig. 6

Fig. 1. *Soluble carboxymethylated mercerized cotton fiber mounted in 95% alcohol. Magnification, 250 ×.* Fig. 2. *Same fiber in 60% alcohol.* Fig. 3. *Same fiber in 50% alcohol.* Fig. 4. *Same as Figure 3, 5 min. later.* Fig. 5. *Same as Figure 3, 10 min. later.* Fig. 6. *Same as Figure 3, 15 min. later.*

ordinary cotton is treated with cuprammonium solution. The fiber broke into pieces, and although most of it went into solution, some remnants of the primary wall and other insoluble fragments remained.

The swelling which occurred in 60% alcohol was probably sufficient to cause weakening of the fiber structure, with resultant loss in breaking strength and increases in fiber diameter to give increased yarn thickness. Some gelatinization of carboxymethylcellulose probably occurred which on drying hardened on the surface of the fibers and yarns causing a starch-like stiffening. Accordingly, in the neutralization and washing steps in the process, 95% alcohol must be used. This makes possible the production of samples with a soft hand which retain from 90% to 95% of their breaking strength and which undergo only a slight increase in thickness.

Figures 7 to 9 show views of a longitudinal section of a single water-soluble cotton fiber prepared from raw cotton thread which was boiled in monoethanolamine prior to carboxymethylation. In this case, the swelling was not uniform along the fiber axis, but rather the fiber seemed to break into short segments which dissolved quickly and completely even in 50% alcohol. The time interval between Figures 8 and 9 was very short, and a few seconds after the photograph in Figure 9 was taken there were no visible remnants of the fiber.

Effect of Neutralization with Mineral Acids

Because of the impracticability in commercial practice of using acetic acid for neutralization of alkali, mineral acids were substituted, and their effect upon the breaking strength and carboxymethyl substitution of the final products was determined.

Three skeins of 7/2 mercerized cotton thread were treated in the usual manner with 15% monochloroacetic acid solution, centrifuged, and soaked in 50% sodium hydroxide solution for ½ hr. After centrifuging, the skeins were neutralized with 2% alcoholic solutions of sulfuric, hydrochloric, and acetic acids, respectively. The samples were washed thoroughly with 95% alcohol and dried in air at room temperature.

The neutralizations with the two mineral acids produced a large amount of precipitated sodium salts which were rather difficult to wash out with alcohol. Acetic acid gave no visible salt precipitate, but did not neutralize the sample as quickly as the stronger acids.

The samples were re-treated with 50% monochloroacetic acid followed by 50% sodium hydroxide to produce the soluble form, and the effect of the three acid washes was again observed. The same effects were obtained as with one carboxymethylation treatment. The samples washed with mineral acid were in the free acid form and were not soluble in water but were soluble in dilute alkaline solutions. The acid form may be converted to the water-soluble sodium form by treatment with alcoholic sodium hydroxide. The acetic acid-washed sample

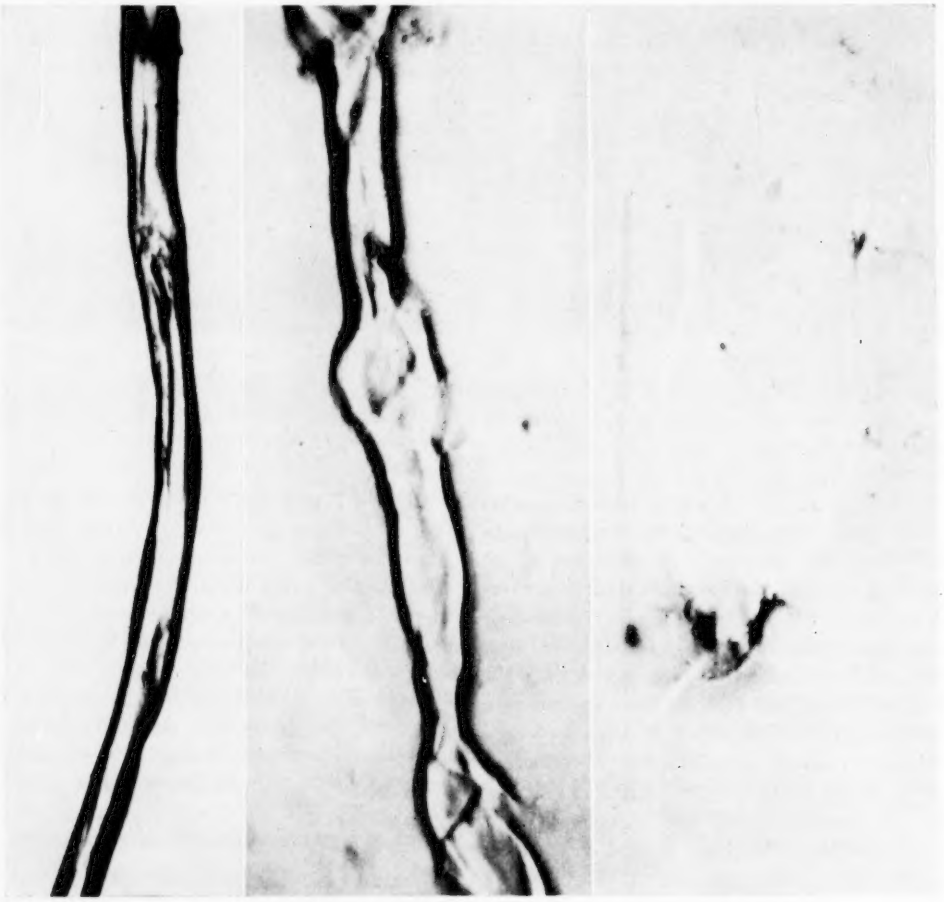

FIG. 7 FIG. 8 FIG. 9

FIG. 7. *Soluble carboxymethylated cotton fiber, made from monoethanolamine-extracted cotton, mounted in 95% alcohol. Magnification, 400 ×.* FIG. 8. *Same fiber in 50% alcohol.* FIG. 9. *Remnants of fiber, a few seconds after Figure 8.*

remained as the sodium salt and was soluble in distilled water.

Table II shows the breaking strengths and carboxymethyl substitutions of the samples after the first step and after the second step of treatment. It is apparent that there were no significant deleterious effects from the mineral acid washing on the breaking strength of the threads.

Characteristics of Products

Moisture Regain

Several batches of soluble cotton thread were prepared by the two-step treatment. When these were neutralized with acetic acid, given an alcoholic ammonium hydroxide wash, and stored several weeks in the laboratory, they became moist and lost much of their breaking strength.

Two theories were advanced to explain this condition: either the washing in alcohol was not sufficiently thorough to remove residual ammonium acetate, known to be hygroscopic, or the treated cotton itself may have some increased affinity for atmospheric moisture, or both.

To test these theories, an investigation was made of the moisture regain of the carboxymethylated cotton in the form of the ammonium and sodium salts and the free acid. The three kinds of treated cotton and a mercerized control were washed thoroughly in hot alcohol, centrifuged, dried at 105°C for 2 hrs., and placed in a vacuum desiccator over calcium chloride overnight. The samples were weighed and then exposed to the air in a constant temperature-humidity room at 70°F and 65% relative humidity. They were weighed periodically for 48 hrs. As shown in Figure 10 the sodium salt gained 12.4%, the ammonium salt 11.7%, and the free acid 10.4%. The mercerized control gained 6.9%.

TABLE II. EFFECT OF ACID NEUTRALIZATION ON THE BREAKING STRENGTH AND SUBSTITUTION OF CARBOXYMETHYLATED COTTON THREAD

Acid wash solution	Carboxymethyl group: anhydroglucose units		Breaking strength*	
	First step	Second step	First step (lbs.)	Second step (lbs.)
2% acetic	1:14	1:3	9.3	8.2
2% sulfuric	1:17	1:3	8.7	7.7
2% hydrochloric	1:14	1:3	9.5	8.0

* The untreated thread had a breaking strength of 8.6 lbs.

The hygroscopicity of the ammonium hydroxide-treated samples was attributed to the first of the two theories mentioned—*i.e.*, incomplete washing of the samples in alcohol. Subsequent analysis demonstrated the presence of ammonium acetate in the original samples.

Solubility

Most of the samples given the two-step treatment were prepared, for convenience, from alcohol-extracted raw cotton or mercerized cotton. It was observed that, regardless of the amount of carboxymethyl substitution in the treated samples, there was always a residue which remained after the fibers had completely disintegrated in water. Tripp *et al.* reported [8] that only about 50% of the primary wall of a cotton fiber is cellulose, and it was assumed from observation of the dissolution of fibers under the microscope that this residue is composed of that part of the primary wall which is of noncellulosic material.

According to Tripp [9] the noncellulosic material of the primary wall can be removed either by pressure-kiering the cotton in 2% sodium hydroxide solution or by boiling in monoethanolamine. Two samples of raw cotton and two samples of mercerized cotton were given each of these treatments prior to the two-step carboxymethylation, and their solubility characteristics in water were observed. Products of the two raw cotton samples dissolved almost completely in water. Surprisingly, however, prod-

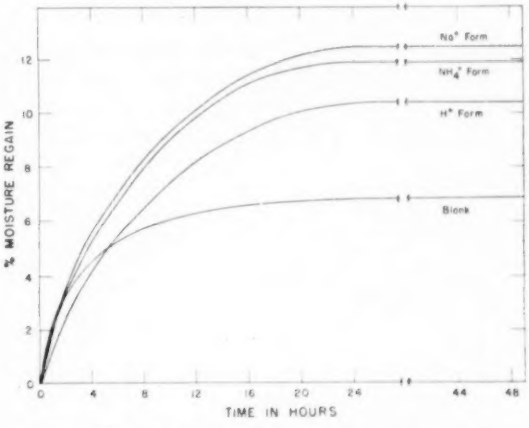

FIG. 10. *Moisture regain of various forms of carboxymethylated cotton.*

ucts of the mercerized cotton disintegrated in water but left a residue of particles which did not dissolve.

Consideration of these findings led to the conclusion that in mercerized cotton the outer layers of the secondary wall are under rather severe tension. This inhibits the intramicellar swelling necessary for carboxymethylation of these layers, and therefore prevents sufficient reaction for complete solubility. The effect is essentially the same as that reported by Hess and Trogus [5] in their work on the mercerization of cotton under tension. In Table I it may be pointed out that the sample which had been mercerized under tension did not carboxymethylate to as great an extent as the other pretreated samples. Consequently, for optimum solubility, cotton which is to be treated by the two-step carboxymethylation process should first be purified by pressure-kiering or by boiling in monoethanolamine prior to carboxymethylation.

Summary and Conclusions

Cotton in the form of sliver, yarn, and thread was carboxymethylated with monochloroacetic acid and sodium hydroxide solutions in either a one-step or a two-step process to give products which disintegrate or dissolve in water. Complete water-solubility was obtained in cotton which was first pretreated by pressure-kiering in 2% sodium hydroxide solution or boiling in monoethanolamine before being given the two-step carboxymethylation. Some of the excess alkali used in the process was removed by alcohol washing, and the remainder was neutralized with acid in alcohol.

When strong acids, such as hydrochloric and sulfuric, are used in the neutralization process, the free acid of carboxymethylcellulose, which is insoluble in water but soluble in dilute alkaline solutions, is formed. Acetic acid, however, does not remove the sodium ion from the sodium carboxymethylcellulose, which is soluble in water.

Soluble cotton in the form of sliver tends to be harsh and has high friction characteristics. These defects can be overcome by treatment with lubricants or softening agents in solutions of acetone or alcohol. Lubricated soluble cotton sliver was spun into yarn on a small scale without difficulty, and a mixed cloth was woven with plain and treated yarn.

Acknowledgments

The authors are indebted to Ruth Giuffria and Anna T. Moore for photomicrographs; to Janice M. Poynot for breaking strength determinations; to Verne W. Tripp for helpful suggestions; to members of the Cotton Mechanical Processing Division for the spinning of yarns and the weaving of fabrics from soluble cotton; and to Julius R. Jung, Jr., for drawing Figure 10.

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Ultrasonic Treatment of Lint Cotton

A. E. Martin, Jr.

Southern Regional Research Laboratory, New Orleans, Louisiana*

Introduction

Increasing quantities of mechanically harvested and other trashy cottons have emphasized the limitations of existing textile cleaning methods and the need for improved cleaning procedures. As part of its research on cotton processing methods and machinery, the Southern Regional Research Laboratory has given consideration to the fundamental physical methods of electrostatics, mechanics, and ultrasonics in search of a promising cleaning system. This paper reports some preliminary investigations of the effects of ultrasonic radiation on lint cotton treated in relatively large samples.

A survey of the literature indicated a variety of interests in the use of sonic and ultrasonic radiation in cellulose research. Buckingham [3] investigated effects in pulp suspensions at 0.3 kc. and 1.2 kc. Simpson and Mason [8] in similar studies found no evidence of chemical degradation following irradiation periods of 1 hr. at 500 kc. Mechanical damage—*i.e.*, fibrillation and ballooning—has been noted by Wuhrman, Heuberger, and Muhlethaler [9] in attempts to reconcile particle size and viscosity theory. Morehead [6] irradiated hydrolyzed and nonhydrolyzed cellulose and compared the particles so obtained. Forziati and coworkers [4] attempted without success to use sonic radiation at 8 kc. to prepare cotton powder for infrared transmission spectroscopy. Schmid [7] and Melville and Murray [5] were able to demonstrate ultrasonically induced macromolecular degradation at low frequencies and low concentrations.

At the Southern Regional Research Laboratory it was felt that ultrasonic treatment of relatively large samples of lint cotton would be of interest from the standpoint of possible physical and chemical property modification, and possible discriminatory effects between lint cotton and its attached foreign matter or "trash." Accordingly, a strict low middling cotton (Rowden variety, 31/32 in. staple length) was treated at nominal frequencies of 400 kc., 500 kc., and 800 kc. Sound wave lengths in both water and cotton at these frequencies are compared with fiber dimensions in Table I. Young's modulus for cotton was taken as 5×10^{11} dynes/cm.^{2} in obtaining the data given.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Experimental

The ultrasonic transducers employed were barium titanate cylinders (Brush Development Co., Ceramic A*) resonated in thickness mode to give a radially focused sound field. The transducers were driven by a modified radio-frequency transmitter capable of running 400 watts input to the power amplifier. Samples of cotton of 15 g. each were loaded into the transducer cylinder and completely immersed in a 0.1% Decerosol OT solution in distilled water.

Reliable direct measurements of acoustic energy densities were not readily obtainable. A crude rate-of-temperature-increase method was employed to estimate the energy densities. Comparison of data so obtained was made with calculated values based on power input to the power amplifier and conservative conversion efficiencies for both transmitter and transducers. With this technique, acoustic energy densities employed were estimated to be approximately 1 watt/cm.^{2} at the transducer surface.

* The mention of trade products or companies does not imply that they are endorsed by the Department of Agriculture over similar products not mentioned.

TABLE I. RATIOS OF FIBER LENGTH, L, AND DIAMETER, D, TO SOUND WAVE LENGTHS IN COTTON, λ_c, AND IN WATER, λ_w

Frequency (kc./sec.)	L/λ_c*	L/λ_w	D/λ_c*	D/λ_w
400	1.9	6.8	$.77 \times 10^{-2}$	2.7×10^{-2}
500	2.3	8.5	$.91 \times 10^{-2}$	3.3×10^{-2}
800	3.7	13.6	1.5×10^{-2}	5.4×10^{-2}

* Diameter, for order of magnitude, was assumed to be 10^{-3} cm.; fiber length, 2.5 cm.

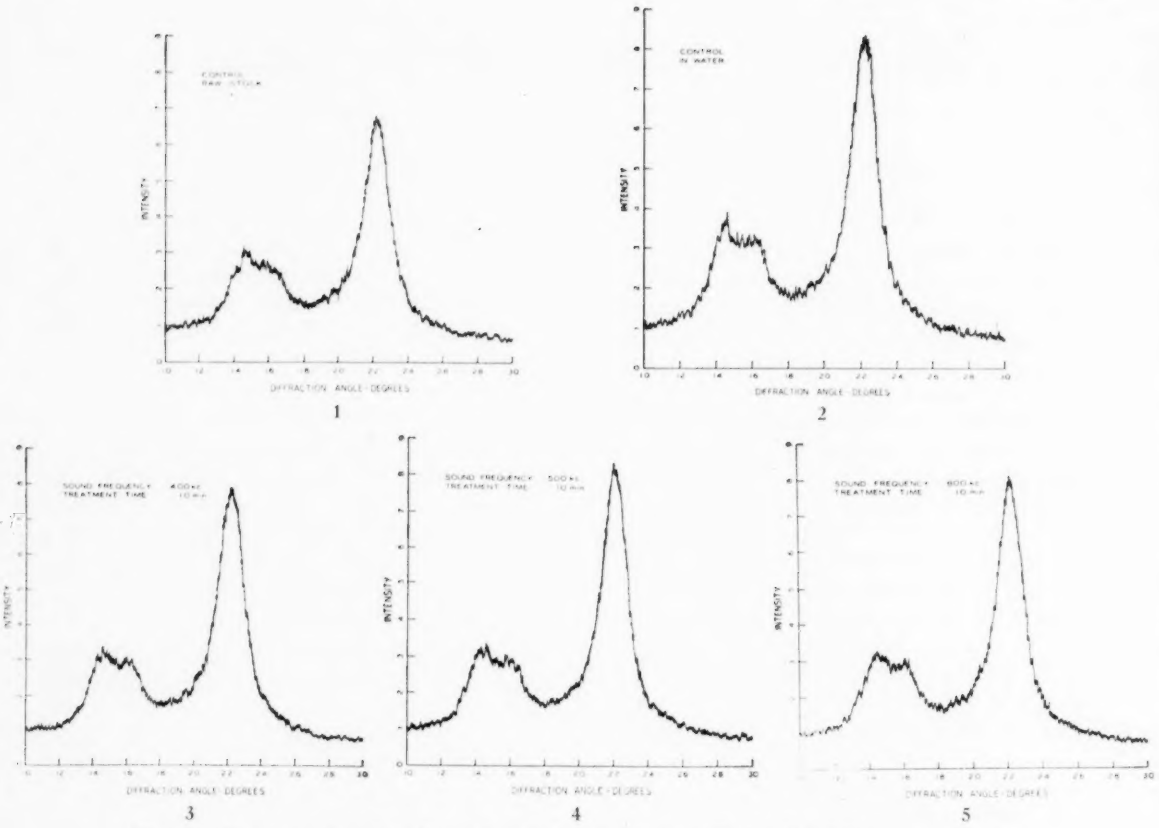

FIG. 1. *X-ray equatorial tracings of control and ultrasonically irradiated lint cotton samples.*

Treatment times ranged from 2.5 min. to 10 min. at each frequency. At the end of each run the sample temperature was checked and found to have risen no higher than 80°C. Control samples in Decerosol OT solution were heated to 80°C to place all samples on the same thermal-effect basis.

Following recommended A.S.T.M. procedures [1], Pressley index, Fibrograph staple length, and Micronaire fineness were determined for raw stock, controls, and treated samples. Mechanical damage was investigated by microscopic examination; degradation was tested by cuprammonium fluidity determination; and crystallinity change was investigated by x-ray diffraction.

During the progress of the work it was indicated that some changes in crystallinity might be occurring. Several samples of amorphous cellulose prepared by vibratory ball-mill grinding were treated at 500 kc. for times up to 20 min. Comparisons were made with appropriate controls.

Results

The results of tests on physical properties are summarized in Table II. It will be noted that no significant changes occur in fineness, length, or strength. The small fluctuations are less than normal experimental error and within the variability of the raw stock itself.

Microscopic examination showed no evidence of fiber damage. Fibrillation and ballooning were not observed, which bears out an opinion [2] offered that such changes in native cellulosic material would require intensities of 4 to 10 watts/cm.^{2} Degradation tests, as determined by cuprammonium fluidities, were negative, as shown in Table III. Representative x-ray equatorial tracings are shown in Figure 1. It appeared, in the case of the lint cotton samples, that there was a slight increase in crystallinity in the sample treated at 500 kc. Higher intensity treatment is needed in order to say definitely that increased crystallization can be induced ultra-

TABLE II. PHYSICAL PROPERTIES OF ULTRASONICALLY TREATED COTTON

Frequency (kc./sec.)	Time of treatment (min.)	Fineness, Micronaire (μg./in.)	Length, Fibrograph U.H.M. (in.)	M.L. (in.)	U.R. (%)	Strength, Pressley index
400	10	5.2	0.94	0.74	79	7.5
400	5	5.2	0.94	0.73	78	7.7
400	2.5	5.2	0.93	0.72	77	7.6
500	10	5.2	0.93	0.71	76	7.5
500	5	5.2	0.92	0.72	78	7.6
500	2.5	5.1	0.93	0.72	77	7.6
800	10	5.3	0.95	0.76	80	7.5
800	5	5.2	0.96	0.77	80	7.5
800	2.5	5.3	0.95	0.76	80	7.7
Control	—	5.1	0.94	0.74	79	7.6
Raw stock	—	5.1	0.95	0.74	78	7.4

TABLE III. DEGREE OF POLYMERIZATION

Frequency (kc./sec.)	Time of treatment (min.)	Cuprammonium fluidity (0.5%) (rhes)	Degree of polymerization
400	10	2.46 ± 0.02	4710
500	10	2.51 ± 0.02	4641
800	10	2.64 ± 0.02	4493
Control	—	2.60 ± 0.01	4521
Raw stock	—	2.49 ± 0.01	4667

sonically. This is borne out by the results in the amorphous cellulose samples as shown in Figure 2. Obviously some recrystallization occurred, but it appeared to be of the same order of magnitude as the control in Decerosol OT.

In an attempt to show mechanical changes in trash, a hand-picked sample of leaf and pepper trash of about 3 g. was mixed with 25 cm.^{3} of 0.1% solution Decerosol OT. This mixture, in a test tube, was placed along the axis of the 500-kc. transducer and irradiated for 2 hrs. using oil coupling. A careful examination of the treated sample revealed no damage and no reduction in particle size. A cloudy suspension was found in the solution, indicating that some foreign matter was removed from the sample; the amount, however, was too small to be of practical interest.

Conclusions

1. At the frequencies and energy densities employed, no mechanical damage was induced in lint cotton; this is in contradiction to previously stated results. No cell-wall damage and no fibrillation or ballooning was induced in bulk samples. This lack of damage is attributed to attenuation and interfacial energy loss and to the fact that the cotton

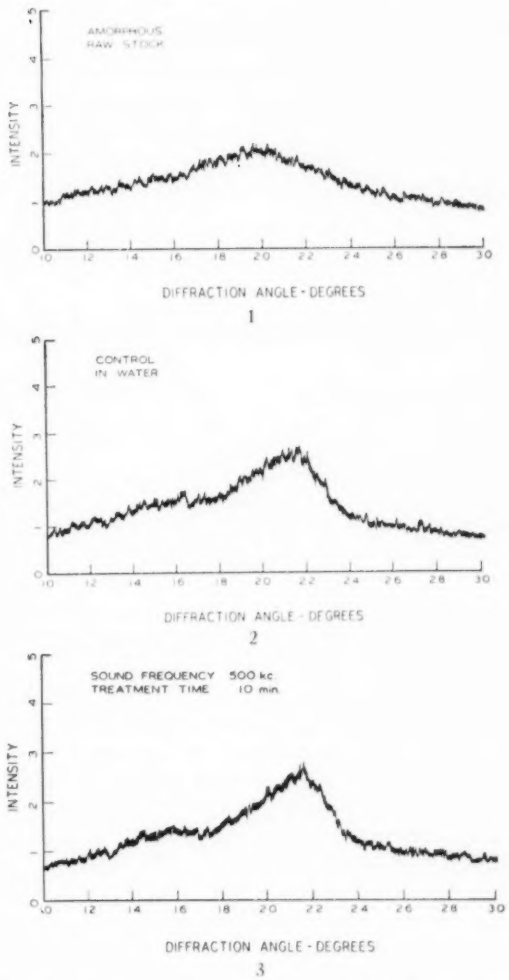

FIG. 2. *X-ray equatorial tracings of control and ultrasonically irradiated amorphous cellulose samples.*

treated in these experiments had no pretreatment of any kind.

2. Any degradation sonically induced in cellulose is immeasurable; this is in agreement with results of other workers.

3. Evidence of crystallinity change was present to a small degree. Further work at higher energy levels at the same and lower frequencies is needed to substantiate this finding.

4. No damage to foreign matter commonly attached to lint cotton was observed. Neither was there any evidence that sound of the frequencies and energy level employed would be useful in effecting the separation of such material from lint cotton.

Acknowledgment

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Observations on the Compressibility of Pile Fabrics*

P. Larose

Division of Chemistry, National Research Council, Ottawa, Canada

A RECENT ARTICLE by Bogaty *et al.* [1] on the thickness-pressure relationships of fabrics has led us to re-examine the results of similar work which we carried out on a number of fabrics during the last war. At that time our main interest, as regards compressibility, was in felts and pile fabrics, but other types of fabrics were also tested. The results of this investigation were re-examined, and we have tried to fit our data to the equation suggested by Bogaty *et al.* [1]. At the same time, we have applied equations proposed by other workers in order to find how suitable they might be to represent the data on hand. In view of the wide interest in fabric properties being shown today, an interest which arises largely from the introduction of new synthetic fibers, we deemed it desirable to publish the results of our effort in this direction.

* This paper is designated N.R.C. No. 3084.

Experimental Procedure

Compression tests were performed by various methods. The Schiefer compressometer [4] with a 3-in.-diameter foot was used in most experiments, but some tests were carried out with a smaller foot of 1 in. diameter. Some measurements were also made using glass plates with surfaces of 7.1, 10.0 and 356 sq. in., and to which weights were added to make up the load to the desired value. The thickness itself was determined by means of a travelling microscope focussed at different places around the plates, and the mean value was taken as the thickness of the fabric. Since the time of compression was a factor in determining the thickness measured, the general procedure was to apply each load for 1 min. before taking a reading. This interval was found to be sufficient to eliminate most of the variation in thickness with time.

In some experiments, the fabrics were subjected to repeated compression and relaxation cycles and the thickness was determined after a given number of cycles, but the results obtained under such conditions will not be discussed in this paper.

Results

The number of fabrics tested and the number of determinations made were so many that it would serve no useful purpose to report all our results here. It will be sufficient to choose a few characteristic examples to indicate the order of the changes observed and the extent to which the various equations proposed to represent compressibility can be applied to our data.

When the tests were performed, it was found that within the range of pressures of interest to us at that time, the results were well represented by the equation

$$t_o - t_p = A \log p,$$

where t_o is the thickness at a pressure of 1.0 lb./in.^{2}, t_p is the thickness at pressure p, and A is a constant for any one particular fabric. This relationship was found to hold fairly well for pressures of 0.1 to 1.0 lb./in.^{2} or more. Tests have shown that in the course of wear (sitting down) by a member of an aircrew, the compression loads to which the clothing is subjected seldom exceed 1.0 ft./in.^{2}

A large number of tests were made on double-pile fabrics which were used as lining in airmen's flying suits. This type of fabric had a ¼-in. wool pile on both sides of a cotton ground fabric. Figure 1 shows the relation between thickness and the logarithm of pressure for two such fabrics, one of which had been removed from a worn flying jacket. The measurements for curves A and B were not carried beyond a pressure of 1.0 lb./in.^{2}, but curve C shows that the equation given above holds for pressures up to about 3 lbs./in.^{2} in the case of this sample. The relationship was found to be equally good for other types of fabrics, such as overcoatings, felts, and certain knitted materials. It failed, however, to represent the behavior of wool or cotton batting.

The equation

$$p = k(t_o - t_p)^\alpha,$$

where k, t_o, and α are constants and t_p is the thickness at pressure p, has been claimed by Hoffman and Beste [3] to fit their data quite well, α having a value of about 5/4 at low pressures and of about 3 at high pressures. Application of their equation to our data failed to give a straight line when log p was plotted against log $(t_o - t_p)$, although in some cases the relationship between the two could be considered linear within a narrow range of pressures. For example, with one fabric the line was sufficiently straight between 0.03 and 0.10 lb./in.^{2} However, the slope was 1.7 with one value of t_o and 1.9 with another arbitrarily chosen value of t_o. The value of α given by the slope of the line is therefore quite different from the values given by Hoffman and Beste. The deviations from the straight-line relationship were larger at the higher pressures, but it was noticed when studying the pressures between 0.1 and 1.0 lb./in.^{2} that with some of the double-pile fabrics the line joining the first two points corresponding to pressures of 0.1 and 0.2 lb./in.^{2} had a slope of 5/4, which is that given by Hoffman and Beste for low pressures. With another type of material (overcoating), the relationship was fairly linear between 0.025 and 0.25 lb./in.^{2} The

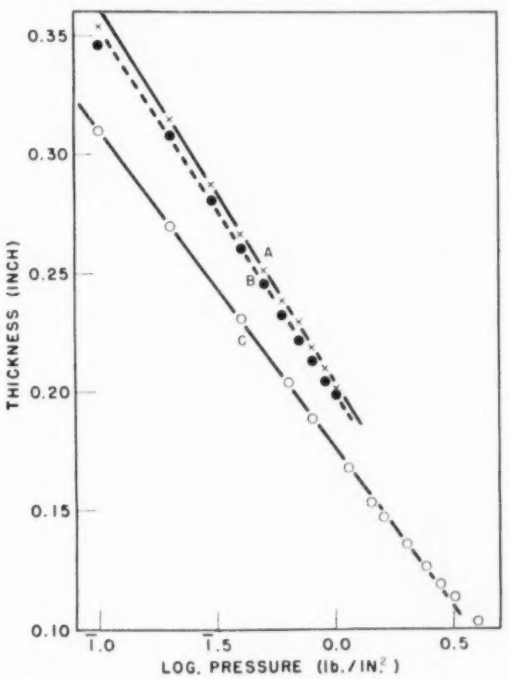

FIG. 1. *Relation between thickness and logarithm of pressure for two double-pile fabrics. Curve* A *is for a worn double-pile fabric;* B *is the same after five compression and relaxation cycles;* C *is for a new pile fabric.*

slope of these lines, however, depends on the value chosen for t_o and the shape of the curve does not change appreciably when t_o is varied over a wide range of values.

Peirce's formula

$$t_p = t_o e^{-xp},$$

mentioned by Hoffman and Beste, was also applied to our results with no success. In no case was a linear relationship found between $\log t_p$ and p, except over a very limited range of pressures.

Other equations which we investigated were those of the Eggerts [2] and van Wyk [5]. These two equations were originally designed to represent the compressibility of a mass of wool fibers, and they are essentially of the same form.

The Eggerts' equation,

$$p_o = (p + p_o)\left(\frac{v}{v_o}\right)^{\alpha},$$

can be reduced to the form

$$p + p_o = \frac{C}{v^{\alpha}},$$

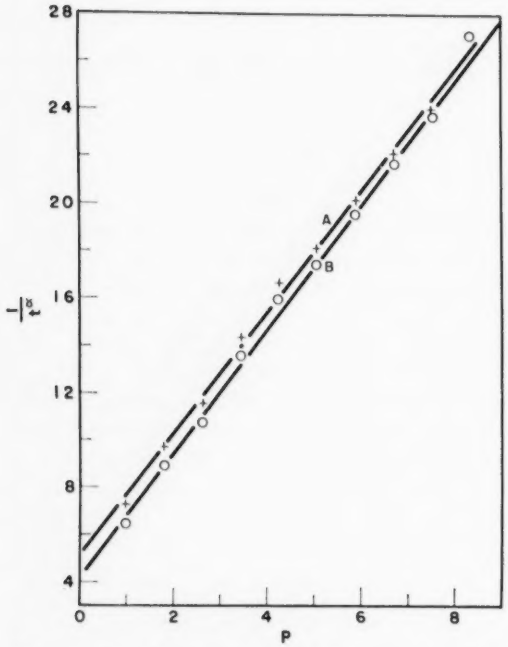

FIG. 2. *The Eggerts and van Wyk equation applied to a double-pile fabric. In* A, $\alpha = 2.3$; *in* B, $\alpha = 2.5$. *The values of* $1/t^{\alpha}$ *for* B *have been multiplied by 3/4 in order to have the same scale of ordinates for* A *and* B.

where $C = p_o v_o^{\alpha}$ = constant, v refers to the volume of the fibrous mass under pressure p, and v_o is the initial volume corresponding to a "latent pressure" p_o.

van Wyk's equation is

$$p = \frac{KYm^3}{\rho^3}\left(\frac{1}{v^3} - \frac{1}{v_o^3}\right),$$

where m is the mass, ρ is the density of the fiber, Y is Young's modulus of elasticity, and K is a constant. The equation can be rewritten

$$p + K' = \frac{K''}{v^3},$$

where $K' = \frac{K''}{v_o^3}$ and $K'' = \frac{KYm^3}{\rho^3}$. Both equations are therefore linear with respect to p and $\frac{1}{v^{\alpha}}$ for any given mass of fibers, where $\alpha = 3$ in van Wyk's equation.

Under the conditions of test used to determine the compressibility of the fabrics, the sample can be regarded as a mass of fibers in which the area in a plane parallel to the compressometer foot remains constant but the thickness varies. In applying the above equations to fabrics, v can be replaced by t.

When fitted to the experimental results obtained with the pile fabrics, this form of equation was found to be quite good when the value of α was 2.3–2.6, the best value of α depending on the particular sample tested. However, a difference of 0.2 in the value of α did not make much difference in the fit, and a value of 2.5 can be taken as a general one for the double-pile fabrics studied. Figure 2 illustrates the rela-

TABLE I. TEST OF THE EQUATION $(p + c)(t - a) = b$*

	Overcoating		Double-pile fabric	
$p+0.05$	$t-0.076$	$b\times10^3$	$t-0.160$	$b\times10^2$
0.050	0.034_0	1.70	0.365	1.83
.056	$.029_0$	1.62	.356	2.00
.062	$.025_5$	1.58	.349	2.16
.074	$.021_5$	1.59	.330	2.42
.087	$.019_5$	1.70	.321	2.79
.099	$.018_0$	1.78	.309	3.06
.111	$.016_5$	1.83	.298	3.31
.123	$.015_0$	1.85	.288	3.54
.135	$.014_0$	1.89	.279	3.77
.148	$.013_0$	1.92	.271	4.01
.160	$.012_0$	1.92	.261	4.18
.172	$.011_5$	1.98	.252	4.34

* c = 0.05 lb./in.²; a = thickness under 2.0 lbs./in.² pressure (0.076 in. for the overcoating and 0.160 in. for the double-pile fabric).

tion between p and $1/t^a$ for such a fabric, where a has been made equal to 2.3 in one case and to 2.5 in another.

The final equation which was applied to our data is that proposed by Bogaty *et al.* [1]:

$$(p + c)(t - a) = b.$$

Here, a, b, and c are constants. Bogaty *et al.* chose 0.05 lb./in.^{2} for the value of c and the thickness under a pressure of 2.0 lbs./in.^{2} for the value of a. The value of b was a characteristic of the sample. These authors found that the results obtained at low pressures, up to 0.1 lb./in.^{2}, were fairly well represented by such an equation, but at higher pressures the equation did not hold so well. We have tried to fit our data to the same equation but with little success, even at low pressures. Table I gives the value of b over a pressure range for an overcoating and for a double-pile fabric. It may be noted that b is not constant. The discrepancy at higher pressures is even more pronounced.

It is possible by a slight change in a to obtain a constant value for b in the case of the overcoating, but not with the double-pile fabric. By making $a = 0.079$ in., the value of b for the overcoating remains constant within $\pm 6\%$ of the mean. However, if the value of c as well as that of a is changed and adjusted arbitrarily, it is generally possible to attain a constant b over a wide range of pressures.

Table II gives the results obtained with a double-pile fabric. Different values of a and of c have to be chosen for samples tested under different pressure conditions, but Table III shows that when compared under the same conditions all four samples give almost the same value of b.

Table IV gives the results of a similar calculation for a loose mass of kapok fibers in the form of padding used as coat lining. These data obey the equation provided proper values are chosen for a and c.

TABLE II. THICKNESS-PRESSURE RELATIONSHIP FOR FOUR SAMPLES OF DOUBLE-PILE FABRIC TESTED OVER VARIOUS PRESSURE RANGES

Pressure (lbs./in.^{2})	Thickness (in.)	Calculated b
Sample A: $(p + 0.21)(t) = b$		
0.003	0.582	0.124
0.008	0.560	0.122
0.012	0.542	0.126
0.026	0.510	0.121
Sample B: $(p + 0.24)(t - 0.100) = b$		
0.012	0.593	0.124
0.019	0.585	0.125
0.027	0.563	0.124
0.035	0.547	0.123
0.042	0.539	0.124
0.050	0.526	0.123
0.057	0.519	0.124
0.065	0.506	0.124
0.072	0.498	0.124
0.080	0.490	0.124
0.088	0.482	0.125
0.095	0.470	0.124
0.103	0.461	0.123
Sample C: $(p + 0.34)(t - 0.150) = b$		
0	0.593	0.151
0.006	0.580	0.149
0.012	0.572	0.149
0.024	0.558	0.149
0.037	0.546	0.149
0.049	0.535	0.150
0.061	0.525	0.150
0.073	0.513	0.150
0.085	0.505	0.151
0.097	0.496	0.151
0.110	0.486	0.151
0.122	0.477	0.151
Sample D: $(p + 0.44)(t - 0.068) = b$		
0.00	0.544	0.209
0.02	0.527	0.211
0.08	0.482	0.215
0.16	0.432	0.218
0.31	0.367	0.224
0.46	0.317	0.224
0.62	0.276	0.220
0.77	0.250	0.220
0.92	0.228	0.218
1.08	0.212	0.219
1.23	0.199	0.219
1.39	0.187	0.218
1.54	0.178	0.218
1.93	0.161	0.220
2.31	0.148	0.220
2.70	0.138	0.220
3.08	0.131	0.222
3.46	0.125	0.222
3.85	0.120	0.223
4.24	0.116	0.225
4.62	0.113	0.228
5.01	0.109	0.223
5.39	0.106	0.222
5.77	0.104	0.224
6.15	0.101	0.218
6.55	0.098	0.210
6.93	0.096	0.207
7.31	0.095	0.209

Discussion

The equation

$$t_o - t_p = A \log p,$$

which we have used to represent the behavior of double-pile fabrics is purely empirical and does not appear to be suitable for very loose materials, since it failed to represent the compressibility of wool or cotton batting. It can be applied only to a limited range of pressures.

The equation

$$p = k(t_o - t_p)^{\alpha},$$

proposed by Hoffman and Beste [3], is also empirical and of limited application, since the coefficient α at low pressures is different from that at high pressures. It is evident from this that there must be an intermediate pressure range in which the value of α changes. Moreover, our tests have shown that the value of α depends on the type of fabric. Another weak point of this equation is that t_o can be varied over a fairly wide range of values without changing appreciably the shape of the curve that shows the relation between pressure and thickness. The estimation of t_o from the equation is, therefore, subject to a large error.

Peirce's formula,

$$t_p = t_o e^{-xp},$$

has already been mentioned as having failed to represent our compressibility results. Hoffman and Beste [3] also noted that their results could not be well represented by the Peirce formula.

The equation of Bogaty *et al.* [1],

$$(p + c)(t - a) = b,$$

is again an empirical one, and it does not represent compressibility over a wide range of pressures unless the constants c and a are given different values for each fabric. It is possible, by adjusting these values, to obtain an equation which satisfies a wide range of pressures, but since each fabric has different values of a and c and since these have to be determined by a process of trial and error, the usefulness of the equation is reduced.

The Eggerts' equation [2] and that of van Wyk [5] can be discussed together since, for all practical purposes, they are of the same form. The Eggerts' equation was derived by drawing an analogy between the compressibility of textile materials and that of gases, an analogy which also formed the basis for the equation of Bogaty *et al.* van Wyk's equation has a theoretical basis, but is limited in its application since a number of simplifying assumptions were made in the derivation. In order to fit our data, it was necessary to change the exponent of t from 3 to a lower one of around 2.5. van Wyk noted that there was a tendency for the coefficient to drop when the fiber length was no longer large in comparison with the element of length (length of fiber free to deflect).

Eggert and Eggert [2] listed the values of α for a number of loose materials they tested and found α to vary between 0.2 and 4.3.

The reason for the failure of all these equations to represent adequately the relationship between pressure and thickness of fabrics is not hard to find. Consideration of what must take place when a fabric is being compressed shows that the process is a com-

TABLE III. THICKNESS-PRESSURE RELATIONSHIP FOR FOUR SAMPLES OF DOUBLE-PILE FABRIC COMPARED AT APPROXIMATELY THE SAME PRESSURE AND USING THE SAME VALUE OF a (0.100 IN.) AND c (0.34 LB./IN.²)

Sample	Pressure (lbs./in.²)	Thickness (in.)	Calculated b
A	0.026	0.510	0.150
B	0.026	0.566*	0.170
B	0.103	0.461	0.160
C	0.103	0.491*	0.173
C	0.122	0.477	0.174
D	0.122	0.454*	0.164

* These values were interpolated from the pressure-thickness curve.

TABLE IV. THICKNESS-PRESSURE RELATIONSHIP FOR A KAPOK PADDING: $(p + 1.5)(t - 0.285) = b$

Pressure (lbs./in.²)	Thickness (in.)	Calculated b
0.00	0.788	0.754
0.25	0.690	0.708
0.50	0.632	0.694
0.75	0.592	0.691
1.00	0.560	0.688
1.25	0.536	0.690
1.50	0.514	0.687
1.75	0.497	0.689
2.00	0.484	0.697
2.50	0.462	0.708
3.00	0.444	0.715
3.50	0.430	0.725
4.00	0.415	0.715
4.50	0.404	0.714
5.0	0.394	0.708
5.5	0.384	0.693
6.0	0.375	0.675

plex one which involves several factors, each of which plays a different role and that to a varying degree, depending on the particular fabric under study. Some of these factors were mentioned by van Wyk. Reference has just been made to the effect of fiber length on the coefficient of t in his equation, but van Wyk also mentioned friction as a possible interfering factor and attributed to it the hysteresis effect he noted. The crimp of the fibers is another factor mentioned by van Wyk.

When pressure is applied to a fabric as it is in a compressometer, several things may take place. There is undoubtedly a deflection of the fibers of the type discussed by van Wyk, where the fibers are regarded as cylindrical beams supported at regular intervals along their length. This leads to the equation proposed by van Wyk for the compressibility of a fibrous mass. During compression, the fibers must take new positions, and in doing so must slip past other fibers at certain points of contact, thus giving rise to frictional effects. The number of such contacts and the effort required to overcome the frictional forces will increase as the fabric becomes denser. Some of the fibers will merely be bent during the process, and this will necessitate a force which is a function of the angle through which the fiber is flexed. Some of the fibers, particularly if crimped, can be regarded as springs being compressed along their length. In addition, there will be some compression of the fibers in a radial direction where fibers are in contact and have a general direction perpendicular to the direction of the force applied. Since most of the fibers in fabrics do lie in such a direction (pile fabrics are an exception), this compressional effect is one which cannot be neglected and which becomes particularly important at the higher pressures, when the density of the fabric is large. The relative importance of each of these factors depends on the type of fiber and the construction of the fabric. It is evident, then, that an equation that would represent adequately the relationship between pressure and thickness would be a complex one containing several terms with a number of constants which would vary with each fabric, and which would depend on the nature of the fibers, the size and twist of the yarns, the tightness and type of weave, the crimp of the yarn, and the crimp, size, and shape of the fibers; even the direction of twist for the relative directions of twist in the weft and in the warp yarn will affect the ease with which the fibers can move under the load applied. One must conclude from these summary considerations that the task of developing an equation of general application to express the compressibility of fabrics is likely to be a hopeless one.

Summary

Six different equations which have been proposed by various investigators to express the thickness-pressure relationship of textile materials have been examined, with particular reference to the compressibility of pile fabrics. The best results are given by a modified form of the equation proposed by Bogaty *et al.* The equations are discussed from the point of view of their utility, and the opinion is ventured that, due to the complex nature of the phenomenon, it is unlikely that a satisfactory equation can be derived to express the compressibility of textile fabrics over a wide range of pressures.

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Change in the Fluorescence of Deltapine-15 Seed Cotton as a Result of Heat*

W. C. Sheehan,† T. L. W. Bailey, Jr.,‡ and Jack Compton**

Institute of Textile Technology, Charlottesville, Virginia

Abstract

Examination of cotton samples in ultraviolet light revealed a variable color fluorescence of the entire bale stock, ranging from violet to blue-violet to ivory-white. Further experiments indicated that the entire fiber mass could be made ivory-white by heating. Unlike commercially ginned fibers, hand-ginned fibers appeared uniformly bluish in ultraviolet radiations, but they could also be made ivory-white on heating.

Experiments were carried out to ascertain whether these heated, white fluorescent fibers had different physical properties from the unheated, bluish fluorescent fibers. Of the various properties examined, only the bending stiffness was found to be different. The heated fluorescent fibers were the stiffer. The cause of this change in fiber fluorescence on heating was found to be associated with the formation of oxycellulose.

Introduction

This investigation of cotton fluorescence had the following twofold objective: to determine why some cotton fibers fluoresce differently from others for reasons other than aging, light exposure, or mildew attack; and to ascertain if there are any differences in the physical properties of fluorescent and nonfluorescent fibers.

Historical Background

Several excerpts from the literature are given here which show that the results the present authors obtained by heating are similar to those witnessed by other observers for cottons degraded by other means.

Pringsheim and Grengross reported that, in general, degradation of cellulose is accompanied by an increase in the intensity of the fluorescence [4].

Many workers have made use of the ultraviolet lamp to differentiate old and used cotton material from fresh material to be used as stuffing in upholstery. The old cotton material generally has an ivory-white color under the lamp. The new material appears blue.

Moskowitz made the interesting observation that used cotton fillings contain small amounts of sulfur dioxide, whereas new fillings do not. The new fillings may be made to show the ivory fluorescence similar to that of the old fillings by fumigating them with sulfur dioxide, by loading them with sulfur compounds, or by exposing the new fillings to air saturated with moisture for over 6 weeks [4].

Winne and Donovan [6] gave the following conclusions: (*1*) As cotton ages, fluorescence turns from a violet to an ivory-white or brownish-white color, with the probable change of cellulose to oxycellulose. (*2*) Pure cellulose produces a violet fluorescence, while oxycellulose gives a strong ivory-white color. (*3*) Fibers from the center of bales of known age had a fluorescence similar to that of new fibers, and those from the outside of the bale showed a very slightly lighter fluorescence. These findings supported the theory that the cotton cellulose changes to oxycellulose with exposure to light, moisture, or air, with an accompanying change in its fluorescence in ultraviolet radiations.

Winne and Donovan gave explanations and experiments similar to the ones presented in the present report regarding the belief that the presence of oxycellulose is the cause of fluorescent change. They reasoned that since cotton waxes and resins are composed primarily of fatty acids, which show a bluish fluorescence, they could play no part in the ivory-

* This paper is a ramification of, and a supplement to, a thesis submitted by W. C. Sheehan in partial fulfillment of the requirements for the degree of Master of Science at the Institute of Textile Technology, Charlottesville, Va.

† Present address: Research Department, Bibb Manufacturing Co., Macon, Ga.

‡ Assistant Technical Director.

** Technical Director.

white fluorescence which occurs on aging. They went further with this by saying that a deeper violet fluorescence was observed and that oxidation proceeded much faster after the oil and wax film had been removed. In solution, the extracted oils and waxes seemed to have a somewhat pale bluish color. In this work it was found that the extracted oils and waxes in solution gave a milky color. This was explained by the fact that a different extraction solvent was used, and that the solution was not placed in a quartz vial for ultraviolet examination.

The presence of oxycellulose in aged cotton was determined by the methylene blue tests and the copper number. The copper number was found by Winne and Donovan to bear a linear relationship to the length of exposure, and it was therefore used by them as a quantitative method for ascertaining the amount of oxycellulose present.

Another experiment which they presented was the exposure of two samples of the same material to direct rays of the summer sun for 3 months. One sample was kept wet, the other dry. Examination under ultraviolet radiations showed that the dry sample gradually lost its fluorescence and at the end of the 3-month period had changed from the violet color of new cotton to the ivory color of old cotton. The sample, wet daily, changed from a deep to a pale violet color. It was believed that the water removed the oxycellulose as fast as formed, and therefore the fluorescent change was only slight. (A decrease in fluorescence was noted after washing a sample which had been sufficiently heated to give ivory fluorescence and allowed to dry in air.)

Cotton Used in This Study

The hand-picked Deltapine-15 cotton grown in Scottsville, Miss., that was used in this study came from blended samples representative of the cotton used by the Institute of Textile Technology in ginning studies. Five wagons of seed cotton, which had been picked on the previous day and stored under shelter, were thoroughly mixed, after which the cotton was weighed and divided into approximately four equal parts for ginning at different combinations of heating and cleaning.

Two samples of the Deltapine-15 are referred to in this work—namely, gin bale #3 and seed cotton. Gin bale #3 represents the cotton that was dried at 400°F (3 driers) without the aid of a lint cleaner. Samples were taken from the press box. The seed cotton samples were taken from each of the five wagons after blending. When hand-ginned samples were used, they consisted of the fibers from 100 seeds, where each seed was randomly taken from a different lock.

Experimental Procedure

Fiber Stiffness

The bending stiffness of cotton fibers was determined by the use of Coplan's modified precision balance [1]. The underlying principle is to determine the amount of force required to bend a given weight of parallel fibers not longer than $\frac{5}{8}$ in. The results are expressed as milligrams of force required to bend a gram of fibers.

From the sample to be tested, ten to fifteen fiber bundles were prepared by taking small, random pinches from several places in the sample. Each of these small fiber bundles, which weighed approximately 50 mg., was parallelized by placing the bundle between the thumb and forefinger of the left hand; with the right hand, the protruding ends were pulled out and the fibers layed back on the bundle. This procedure was continued until most of the fibers were straightened. The fibers were further straightened, however, by holding the tuft thus formed near its mid-point in one hand between the thumb and forefinger, and combing the protruding fibers with a special, coarse hand-comb. The tuft was reversed and the operation repeated. The fibers removed during combing were discarded, and the loose fibers were pulled away from the ends of the tuft and discarded. Combing was continued until all of the fibers in the tuft were parallel. The size of the remaining bundle was not over $\frac{1}{4}$ in. wide and generally did not contain over two or three fiber layers (thickness). A total of 20 strokes with the comber accomplished this; otherwise the original tuft was too large to be analyzed by this method.

The small resulting bundle was then placed in a vise, and the protruding fibers were cut flush with the side faces of the vise. The length of the fibers now in the bundle is equal to or less than $\frac{5}{8}$ in. While the fibers were still in the vise, a spring pin for holding was clamped directly in the center. The prepared tufts were then conditioned for at least 12 hrs., after which they were properly placed in the modified balance. The force required to bend each bundle

(weighing 1 to 2 mg.) was read directly from the face of the balance in milligrams. After bending, each bundle was accurately weighed.

The results obtained by this testing procedure were reproducible.

Other Fiber Properties

Fiber length (Fibrograph), Micronaire fineness, and Pressley strength were determined by standard methods at the Institute of Textile Technology's Physical Testing Laboratory.

Single-fiber breaking strength was determined by breaking 80 to 100 fibers on an Instron type of tester.

Cotton maturities were determined by preferred A.S.T.M. caustic soda method (900 to 1,000 fibers were used for each determination) and by Goldthwait's differential-dyeing technique [2, 3].

TABLE I. FIBER DATA OF DELTAPINE-15

Factor	Method	Unit
Grade	Classer's	SLM*
Fineness (μg./in.)	Micronaire	4.20
U.H.M. (in.)†	Suter-Webb	1.13
Strength (lbs./mg.)	Pressley	7.11
Maturity (%)	Caustic soda	77.50

* Strict low middling.
† Upper-half mean.

TABLE II. FLUORESCENCE *vs.* HEAT

Temperature (°C)	Time (min.)	Fluorescence* Lock *I*	Lock *II*	Lock *III*
98	2	no	no	no
101	4	no	no	no
101	6	no	no	no
120	4	vs	vs	vs
120	6	vs	vs	yes
121	2	vs	vs	vs
121	8	s	s	yes
121	10	s	s	s
121	15	s	s	s
143	2	s	s	s
143	4	yes	yes	yes
143	6	yes	yes	yes
143	8	yes	yes	yes
143	10	yes	yes	yes
165	1	yes	yes	yes
165	2	yes	yes	yes
165	3	yes	yes	yes

* vs—very slight, if any, noticeable difference between heated and unheated samples; s—slight difference between heated and unheated samples; yes—definite difference between heated and unheated samples; no—no difference between heated and unheated samples.

Heating Experiment

The fibers on each seed were fluffed open in order to ensure uniform heat penetration; and three seeds, each from a different lock, were used for each determination. The samples were hung in an air-circulating oven from a copper wire, after which they were heated at temperatures ranging from 98° to 165°C for various intervals of time, 1 to 15 min. The samples were not placed in the oven until the desired temperature had been reached. For each temperature and for each time exposure investigated, a different set of samples was used.

Extractions

All extractions were carried out by use of the Soxhlet extraction apparatus for 6 hrs. in a equimolal ethyl alcohol-benzene mixture.

Oxycellulose Tests

Prussian blue, Turnbull's blue, and Nessler's reagent were used according to the procedures given by Skinkle [5] for the detection of oxycellulose.

Results

The following phenomena, which were investigated in this inquiry, are reported in Tables I to VIII, inclusive: fiber properties of Deltapine-15, fluorescence *vs.* heat, fluorescence of extracted hand-ginned cotton, presence of oxycellulose in fluorescent fibers, maturity and fineness of fluorescent *vs.* nonfluorescent heated cotton seed hairs, bending stiffness, and fiber strength of natural and heated cottons.

TABLE III. FLUORESCENCE OF HEATED AND UNHEATED HAND-GINNED DELTAPINE-15 SEED COTTON BEFORE AND AFTER SOLVENT EXTRACTION

Fluorescence	Heated cotton*	Unheated cotton
Before extraction	ivory-white	bluish-white
After extraction	ivory-white	bluish-white
After extraction, then heating at 165°C for 3 min.	—	ivory-white
Of solvent after extraction	slight milkiness	slight milkiness
Of solvent residue	yellow-cream	yellow-cream
Of residue after heating	In both cases, there appeared to be a slight increase in fluorescence.	

* The samples were heated in a dry-air-circulating oven until the fibers were completely fluorescent in ultraviolet light. A portion of the unheated sample was retained as a standard.

Discussion of Results

The observation that the fluorescence of cotton fibers may be changed by some cause other than those previously mentioned was first made while making use of ultraviolet light for assessing the influence of various gin drying temperatures on nep formation. Fibers having a glittering white fluorescence, in contrast to the bluish fluorescence of the majority of the fibers, were found distributed throughout the samples. Knowledge of the past history of the cotton made evident the fact that fluorescence was not a result of aging, light exposure, or mildew attack.

TABLE IV. Presence of Oxycellulose in Fluorescent Fibers

Test	Natural seed cotton	Heated (fluorescent) seed cotton	Fluorescent fibers from #3 gin bale
Prussian blue	−	+	+
Nessler's reagent	−	+	+
Turnbull's blue	−	+	+

TABLE VI. Maturity of Fluorescent and Nonfluorescent Heated Cotton Seed Hairs

Sample	Total fibers examined	Immaturity (%) (18% NaOH method)
Fluorescent seed hairs heated 121°C, 8 min.	695	6.2
Nonfluorescent seed hairs heated 121°C, 8 min.	527	19.2
Fluorescent seed hairs heated 120°C, 6 min.	446	16.8
Nonfluorescent seed hairs heated 120°C, 6 min.	448	15.0

Curiosity as to whether all cottons contained both ivory-white and bluish fluorescent fibers led to the examination of several cottons. White fluorescent fibers were found to be present in varying amounts in all cases but two: combed Sac cotton and the Deltapine-15 seed cotton. Because these last two cottons had not been exposed to heat (Sac cotton is ginned on a roller rather than a saw gin, and hence

TABLE V. Maturity and Fineness of Fluorescent vs. Nonfluorescent Fibers for Gin Bale #3

Factor	Bulk	Fluorescent
Micronaire reading*	4.20	3.85
Maturity (%) (18% NaOH method)	75.60	77.00
No fibers tested	1609	1516
Cross section	Fluorescent more immature than bulk	
Differential dyeing	77.50	77.50

* Average of two determinations.

TABLE VII. Bending Stiffness

Sample	No. of tests	Ave. bending stiffness (mg. of force/g. of fiber)
1. Natural	2	35
2. Heated (fluorescent) 165°C, 3 min.	2	46
3. Extracted 6 hrs., 1:1 ethyl alcohol-benzene mixture	2	76
4. Extracted, then heated at 165°C, 3 min.	2	76
5. Gin bale #3 fluorescent	5	51
bulk	4	53

TABLE VIII. Fiber Strength of Natural and Hand-Ginned Deltapine-15 Cotton as Compared with the Fiber Strength of Fluorescent and Nonfluorescent Samples Taken from the Same Cotton which Had Been Commercially Ginned*

Factor	Hand-ginned fibers		Gin bale #3	
	Natural	Heated	Bulk	Fluorescent
Pressley index (g./den.)	4.02	3.98	3.90	3.93
Single fiber BS† (g. per fiber, 9.5 mm. gage length)	3.50	3.72	4.21	3.73
Elongation to break (%)	7.04	8.38	8.24	7.78
Information concerning single-fiber strengths				
No. of fibers tested	78	116	101	100
Mean strength (stress units)‡	26	27	31	28
Standard deviation (stress units)	11.3	13.1	13.1	12.5
Significant difference between means at the 10% level**	none		slight	

* The excessive drying temperature used in a commercial gin was 400°F.
† BS—Breaking strength.
‡ 7.42 stress units are equivalent to 1 g. breaking strength.
** The significant difference between means was determined by application of the Student's T distribution.

there is no drying operation), it was proposed in a discussion between the authors that heat may account for this phenomenon of fluorescence.

Heat versus *Fluorescence*

The influence of heat was substantiated by taking hand-picked seed cotton, which was known to have only bluish fluorescent fibers, heating it in an air-circulating oven at 185°F for several minutes, and then subjecting it to ultraviolet light. The results were very fruitful in that all the cotton hairs on the heated seed were ivory-white in fluorescence. In ordinary light, no distinction could be made between the two.

A heating experiment was carried out to find the lowest temperature at which this phenomenon took place, and to see if it was a gradual or a trigger effect. The results presented in Table II show that ivory-white fluorescence occurred in a stepwise fashion until 143°C (4 min.) was reached, after which fluorescence was observed continually. However, there were two cases—120°C (6 min.) and 121°C (8 min.)—in which only one of the three seeds being heated gave a definite fluorescence. This indicates that some fibers are more sensitive to heat than others. The fibers heated at 165°C for 1 and 2 min. appeared slightly yellow under ordinary light. On the other hand, of those heated to 165°C for 3 min., only one of the three showed a yellowish tint. The fluorescence of all the cottons heated at 165°C was no greater than the most fluorescent of those observed at 143°C. The three samples tested at 143°C for 4 min. were not as white in their fluorescent properties as other samples tested at 143°C for longer periods of time, indicating that fluorescence is a function of both temperature and time.

Cause of Fluorescence

Because heat can cause cotton fibers to change their fluorescent properties in ultraviolet light from a blue to an ivory-white, the investigation was carried further in order to determine what effect heat was having on the fiber to cause this change.

It was found that water-soluble impurities played no part in this fluorescent effect. Several samples of the hand-ginned seed cotton were thoroughly soaked in warm distilled water for about 20 min. The bath used was replaced three times, and the samples were thoroughly squeezed before each change. After completion of this procedure, the samples were air-dried, after which they were heated to 165°C for several minutes and then examined in ultraviolet light. There was the same noted change in fluorescent properties.

The possibility of chemical change occurring in the cotton waxes as a result of heating, thus causing the phenomenon, was next examined. Two samples of hand-ginned Deltapine-15 seed cotton were extracted for 6 hrs. in a 1 : 1 ethyl alcohol-benzene mixture. The extracted samples were then divided into three portions: one was retained for a standard, one was heated at 143°C for from 4 to 5 min., and one was heated at 165°C for 2 min. Examination of these specimens in ultraviolet light revealed the ivory-white fluorescence. The extraction solvent was evaporated over a water bath, and the residue showed a yellow-cream fluorescence in ultraviolet light, which appeared to increase after heating at 150°C for 1 min. Heating the waxes and resins below their melting point had no noticeable effect on the intensity of the observed fluorescence.

Next, similar hand-ginned samples were heated at 165°C for 2 min., after which they were extracted for 6 hrs. with a 1 : 1 ethyl alcohol-benzene mixture. The extracted samples were air-dried overnight.

The heated, extracted, air-dried samples still showed the marked ivory-white fluorescence. The cotton waxes and resins were recovered as before by evaporating the solvent over a hot water bath. After heating this residue to the melting point (approximately 150°C), the intensity of fluorescence appeared to increase. When waxes were heated excessively, they had a rusty color in ultraviolet light. Since fluorescence was observed both before and after heated samples were extracted, as well as after extracted samples were heated, it is evident that the cotton waxes and resins play no part in this phenomenon.

It was wondered what effects the presence of grease on the ground-glass connections of the Soxhlet apparatus being used for extraction and the presence of impurities in the solvent were having on the results.

To show that the aforesaid experiment was carried out with sufficient accuracy, the test was rerun. This time, however, a redistilled alcohol-benzene mixture was used for extraction, and all grease was removed from the ground-glass connections of the Soxhlet apparatus. It may be well to mention that before dis-

tilling, the solvent had a milky appearance in ultraviolet light; and a small amount of residue, which resulted from evaporation, appeared pale yellow in color when examined under the lamp. On the other hand, the redistilled solvent was completely devoid of any milky color, and there was no residue obtained on evaporation. Other than the use of the redistilled solvent and the use of the grease-free apparatus, the procedure and samples were the same as before. The results are tabulated in Table III. From these results it is evident that the cotton waxes and resins, even though themselves fluorescent, are not the cause of the ivory-white fluorescence which occurs on heating. This leaves only the possibility that heating causes some physical or chemical change in the cellulose itself, which, in turn, changes the fluorescent properties of cotton fibers.

Three distinct tests for the presence of oxycellulose were made on hand-ginned cotton, unheated and heated, and on fluorescent fibers dissected from gin bale #3. The results given in Table IV show that oxycellulose is present in both oven-heated and ginned fluorescent samples. On the other hand, the unheated cotton gave negative results for all three tests.

It is questionable whether the change in fluorescent properties should be attributed to the oxycellulose per se or to the presence of some degraded material accompanying the formation of oxycellulose. Nevertheless, it is quite apparent that the fluorescent properties of cotton fibers may be distinctly changed as a result of heat degradation.

Physical Properties of Fluorescent Fibers

To determine if any difference existed between the physical properties of fluorescent fibers as a result of heating and nonfluorescent fibers, the following tests were made: fineness, maturity, stiffness, and fiber strength.

Examination of gin bale #3 under the ultraviolet lamp revealed that the fluorescent fibers occurred in clusters and were frequently attached to seed-coat fragments. This led to the idea that certain fibers may be more sensitive to a change in fluorescent properties, and hence to heat degradation. Since it appeared that immature fibers were the more sensitive, several of the heated seed cottons were examined in ultraviolet light after being "butter-flied." The findings showed that the hairs located on that portion of the seed which is known to be predominantly immature had changed to an ivory-white fluorescence, while the remainder of the hairs were bluish-white. To substantiate this observed effect, approximately 7 g. of fluorescent fibers were removed from a representative sample of gin bale #3.

Comparison of the Micronaire reading (Table V) of the dissected fluorescent fibers with the reading of bulk sample (specimens from which the fluorescent fibers had not been removed) showed a significant difference of 0.35, the fluorescent fibers being the finer. The difference would have been even greater if it had been possible to *completely* isolate the fluorescent fibers from the nonfluorescent ones. This would have made the Micronaire reading of the dissected fluorescent sample smaller than that which was obtained. Such a segregation, however, would have taken several weeks. Furthermore, since the bulk sample contained both fluorescent and nonfluorescent fibers, its Micronaire reading was smaller than it would have been had only the nonfluorescent fibers been present. It is estimated that the fluorescent sample contained approximately 25% nonfluorescent fibers. A suggested explanation for the difference in Micronaire readings is that either the fine fibers or the immature fibers or both are more sensitive to excessive heat than coarse mature fibers, and hence change in fluorescent properties more readily. To determine whether fiber fineness or maturity was involved in the explanation, at least for the samples in question, the maturity count was taken by the A.S.T.M. caustic soda method. The results given in Table V show that no significant difference between the maturities of the two samples was obtained after examination of over 1,500 fibers from each specimen. The differential-dyeing technique for the determination of maturity was also used. The results given in Table V showed that both samples were within the 75% to 80% maturity range. There were, however, noticeable color differences between the samples. The fluorescent sample was greener, perhaps because of the presence of finer fibers. Such results do not disprove the possibility that immature fibers may be more sensitive to heat than mature fibers; but, for this specific sample, all evidence points towards the finer fibers being the more sensitive.

For two cases, as shown in Table II, there are apparently anomalous results. In each case, one of the three specimens which constituted the sample fluoresced while the other two did not. Maturity counts showed that in one case the fluorescent fibers were

more mature, while in the other case there was no significant difference. These results are given in Table VI.

The bending stiffness of natural cotton seed hairs, heated cotton seed hairs (165°C, 2½ min.), extracted cotton seed hairs, and extracted heated cotton seed hairs, as well as the stiffness of the fluorescent and nonfluorescent fibers of gin bale #3, was determined by the use of the fiber stiffness tester. Each sample consisted of more than ten specimens, and each test was duplicated. All seed hair samples used for these tests were taken from a laboratory hand-ginned sample of Deltapine-15. The results are given in Table VII.

The results show that when untreated cotton fibers are heated to the point where a change in fluorescent properties occurs, the bending stiffness increases. The fact that there is no significant difference between the bending stiffness of the #3 gin bale samples may be explained by considering two opposing factors which are believed to exist. That is, the fluorescent sample contains primarily fine fibers which would tend to decrease the stiffness; on the other hand, the heating which they have undergone tends to increase their stiffness. The two factors more or less balance each other, causing no significant change in stiffness over the bulk sample. It is believed, however, that if the fibers were heated excessively—possibly until they were scorched—the bending stiffness would be below that of the untreated fibers. In other words, if degree of heating were plotted against stiffness, an inverted horseshoe curve would be obtained. These results also show that fibers which have been extracted and then heated are stiffer than those which have only been extracted. This is significant in that it shows that the stiffness of natural fibers increased on heating because of some change in the cellulose, rather than some change in the waxes or resins.

The fiber strength, given in Table VIII, was determined on natural and heated hand-ginned fibers and fluorescent and nonfluorescent samples from gin bale #3. The tests samples came from the same laboratory samples used for the stiffness determinations. The Pressley index shows no significant difference between the strengths of the four samples (six specimens constituted a sample). The single-fiber break shows no significant difference between the strengths of the natural and heated hand-ginned samples; however, the gin bale bulk sample was appreciably stronger than the fluorescent samples at the 10% level of significance, but not at the 1% level.

Summary and Conclusions

1. The fluorescent properties of untreated cotton in ultraviolet radiations change from a bluish white to an ivory-white on heating. This fluorescent color change is similar to that reported by investigators for the aging of cotton.

2. Because of similar fluorescent properties between old and heated cotton, the tests for distinguishing old cotton from new cotton would be in serious error unless the past history of the material were known.

3. The ivory-white fluorescence which occurs on heating is believed to be due to the presence of either oxycellulose or some other degraded material which accompanies the formation of oxycellulose. This belief is based on the following results: (*a*) Water-soluble materials played no part in the noted fluorescent change. (*b*) Cotton waxes and resins, although fluorescent, had no effect on the ivory-white color observed under the ultraviolet lamp, since the phenomenon occurred after extraction of these waxes and resins. (*c*) The ivory-white fluorescent fibers gave positive tests for the presence of oxycellulose, while the bluish fluorescent fibers (untreated) did not. (*d*) The temperature (143°C, 4 min.) at which this ivory-white color was first observed is very close to that cited in the literature for the formation of oxycellulose. (*e*) Washing cotton, which had been heated and then examined in ultraviolet light, appeared to dimish the amount of fluorescence. Low-molecular-weight oxycellulose is soluble.

4. Fine fibers, not necessarily immature, appear to be more sensitive to high temperature, as indicated by a fluorescent change; hence, they are more easily heat-degraded than coarse fibers from the same sample.

5. Heat degradation, which occurred at that point where the fluorescent change was first noted, had no effect on either the fiber bundle or the single fiber strength.

6. The bending stiffness of hand-ginned cotton fibers, which fluoresced as a result of heating at 165°F for 3 min., was greater than the stiffness of unheated fibers.

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A Comparative Study of the Tinius Olsen and Peirce Stiffness Testers

Walter J. Hynek and Gerald Winston

Quartermaster Research & Development Laboratories, Philadelphia, Pennsylvania

Introduction

The hand of a fabric is that complex quality which produces a psychological impression from the stimuli obtained in the touching, squeezing, or otherwise handling of the fabric. These stimuli reflect such properties as flexibility, compressibility, extensibility, resilience, density, surface friction, surface contour, and thermal characteristics [3]. Being nonspecific in nature, hand is quite difficult to measure quantitatively, but attempts have been made. As most textile technologists agree, flexibility is perhaps the most important and the easiest of these properties to measure in the laboratory; the present study is concerned with the measurement of this property.

Not only are stiffness measurements a good index to the hand of a fabric, but they are also a means of determining the effect of finishing operations and chemical treatments on the flexural properties of a fabric. Many of the fabrics used by the Army are chemically treated to provide resistance to fire, water, weather, mildew, and shrinkage. These treatments in many cases consist of surface coatings to the fabrics which result in fiber-to-fiber bonding and give the fabric a harsher hand and an increased stiffness. To control this increase in stiffness within reasonable limits, stiffness values are included in federal specifications for many treated fabrics.

In 1951 a study was made by Abbott [1] in which the subjective evaluation of stiffness was used as the standard with which to compare the results obtained from five laboratory methods of measuring stiffness. The five methods studied were the Peirce cantilever test, the heart-loop test, the Schiefer Flexometer, the Planoflex, and the M.I.T. Drapeometer. The analysis of the results obtained indicated a significant correlation for four of the five methods, with the Peirce cantilever test yielding the best correlation of the four. It was also stated in this study that the Peirce cantilever test is the most convenient to carry out in the laboratory. However, since Abbott in his work did not include the Tinius Olsen tester, which is used extensively by the Army in its specification work and is an accepted A.S.T.M. stiffness test method [2], the present study was conducted to determine the relative merits of these two instruments.

The study was designed to compare the two machines in the following respects: (*a*) similarity or relationship between average measurements of the two instruments; (*b*) precision or reproducibility of stiffness measurements on any one fabric (a good ap-

paratus should produce a small relative spread between the measurements on one fabric); (*c*) sensitivity or relative ability to discriminate among fabrics of varying degrees of stiffness (good sensitivity means that different degrees of stiffness are registered by a spread in the values greater than that attributable to experimental error); (*d*) influence of operator differences on the results; (*e*) ease of operation and speed of obtaining results (if the measurements obtained by both machines are equally reliable, reproducible, and discriminating, then these two factors should be used to judge between the two instruments).

Test Methods and Materials

The materials selected for testing were fifteen cotton fabrics representative of a cross section of weights, weaves, textures, yarn numbers, and other constructional factors. Ten specimens were cut in the warp direction only from each of these fabrics. To eliminate as many variables as possible, the samples were cut so that the same yarns were in both the Tinius Olsen and Peirce samples. The fabrics had been previously desized and alkali-boiled so that the additional variables due to uneven application of sizing would be eliminated.

The Peirce cantilever tests were made on a commercially available instrument [4] shown in Figure 1. In essence, this instrument allows a sample to bend under its own weight to a fixed angle when projected as a cantilever. Mechanically, the fabric sample represents a cantilever beam which is uniformly loaded by its own weight and bends downward until its end reaches a line which makes an angle of 43°

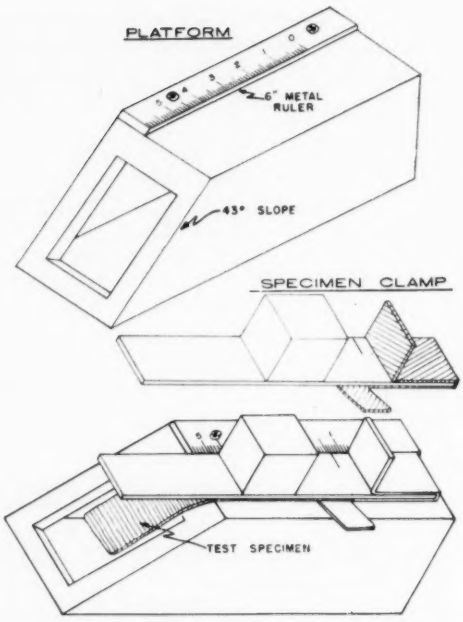

FIG. 1. *Peirce stiffness tester.*

with the horizontal. The longer the projected length, the stiffer the fabric. The apparatus consists of a metal stand with the front tapered off at a 43° angle and a specimen clamp with a 1-in. brass cube screwed to the top. A metal ruler calibrated in tenths of an inch is fastened to the platform at the top of the stand and is used to measure the length of the overhanging sample. A sample 6 in. by 1 in. is placed under the specimen clamp, the end of the sample co-

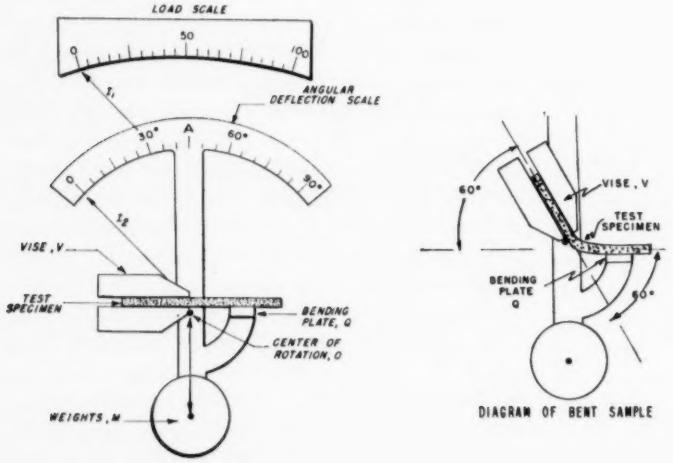

FIG. 2. *Mechanical system of Tinius Olsen stiffness tester.*

inciding with the end of the clamp. The whole assembly, including the sample, is then gradually pushed over the platform, thus allowing the specimen to project as a cantilever from the horizontal platform. Care is taken to prevent relative motion between the clamp and the sample. When the overhanging end touches the 43° line, measurement is taken from the ruler on the instrument to see how far the sample has extended beyond the edge of the platform. This quantity is the length of overhang, L. Using this value in the formula derived by Peirce [5], the bending length, C, is obtained:

$$C = Lf(\theta),$$

where

$$f(\theta) = \left(\frac{\cos \theta/2}{8 \tan \theta}\right)^{\frac{1}{3}};$$

thus

$$C = L\left(\frac{\cos \theta/2}{8 \tan \theta}\right)^{\frac{1}{3}}.$$

The selection of a 43° limiting angle was made to simplify the calculation, for in that case $C/L = f(\theta)$ = approximately $\frac{1}{2}$. Then it is only necessary to take $\frac{1}{2}$ the length of overhang, L, to obtain the bending length, C.

Peirce also defined the flexural rigidity, G, as

$$G = WC^3,$$

where W is the weight per unit area of the fabric. In order to calculate stiffness values in in.-lb. units, as was done in this study, the formula for flexural rigidity is

$$G = W \times C^3 \times 0.482 \times 10^{-4} \text{ in.-lb.},$$

where C is in inches and W is in oz./sq. yd.

The Tinius Olsen tester shown in Figure 2 is a beam-bending type of instrument which involves the bending of a fabric through an angle of 60° and recording the load applied at the bending plate to accomplish this. The fabric sample in this case represents a cantilever beam which is being bent upward by a load that is applied by the bending plate, Q, at a bending span of $\frac{1}{2}$ in. The moment applied by the plate, Q, acts against the stiffness and weight of the fabric sample to bend it. The bending mechanism is shown in the diagram of the bent sample in Figure 2.

The angular deflection, scale A, the pointer indicator, I_1, the bending plate, Q, and the weights, M, are rigidly attached to form a pendulum system pivoted for nearly frictionless rotation about the point O. The fixed load scale measures the deflection of the pendulum system when pressure is applied at Q.

Also rotating about the point O, at the rate of 60° arc/min., is the specimen vise, V, to which is attached the angular deflection pointer, I_2. This vise holds one end of the specimen, while the other end rests on the bending plate, Q, of the pendulum system. As the vise turns in a clockwise direction, the free end of the specimen presses down on Q, thus causing a deflection of the pendulum system, which, as has already been stated, is measured on the fixed load scale by the pointer I_1. The load scale is calibrated to read directly 100 ($L \sin \theta$), where L is the distance between the center of rotation, O, and the center of the applied load, M. Thus, M times the load scale reading divided by 100 gives the bending moment:

$$\text{B.M. (in.-lb.)} = \frac{\text{moment weight} \times \text{load scale reading}}{100}.$$

This calculation is simplified, for each moment weight is stamped with the bending moment it applies when the pendulum is at the maximum angle of swing.

In operation, a 2 in. by 1 in. sample is firmly clamped in the vise. By turning a hand crank, sufficient load is applied to the specimen to show a 1% load reading, and the angular deflection pointer is set to indicate zero angle. The motor is engaged and the load scale is read when the angular deflection scale indicates 60°. The load reading is then reduced by 1%. The stiffness is calculated in terms of bending moment, as shown in the above formula.

Results and Discussion

Table I lists the results of the tests as averages of the ten stiffness measurements obtained by the two testers on each of the fifteen fabrics and a number of statistical analyses. The values obtained by the Tinius Olsen tester are approximately three times as large as, and are closely related to, those obtained by the Peirce tester. This is quantitatively illustrated by the correlation coefficient between the stiffness measurements obtained by the testers—*viz.*, $r = +0.93$; thus the average Peirce stiffness values (in.-lb. $\times 10^{-4}$) can be converted to Tinius Olsen values by the following formula:

$$\text{T.O.} = 3.4 + 3.1P.$$

Figure 3 shows this relationship graphically. Note,

TABLE I. EVALUATION OF AVERAGE WARP STIFFNESS MEASUREMENTS OBTAINED ON THE TINIUS OLSEN AND PEIRCE MACHINES (10 SPECIMENS OF EACH OF 15 FABRICS)

Fabric No.	Fabric weight (oz./sq. yd.) Amount	Rank	Stiffness (in.-lb.×10⁻⁴) Tinius Olsen Amount	Rank	Peirce Amount	Rank	σ_w Precision (in.-lb.×10⁻⁴) T.O.	Peirce	Relative precision $100\left(\frac{\sigma_w}{\text{ave.}}\right) = V\%$ T.O.	Peirce
22	5.8	1	19.6	4	6.4	9	2.9	.8	15	12
30	6.6	2	17.8	2	5.2	4.5	1.4	.7	8	13
23	7.3	3	22.4	8	7.0	11	2.4	1.1	11	15
106	7.8	4	17.1	1	4.2	1	1.2	.2	7	5
109	8.1	5.5	22.5	9	6.1	7.5	1.7	.5	7	8
31	8.1	5.5	21.0	6	6.6	10	1.1	.6	5	10
100	8.4	7	22.0	7	6.1	7.5	5.2	1.0	15	17
103	8.6	8	22.8	10	5.2	4.5	1.3	.6	6	12
104	8.7	9	18.6	3	5.1	3	1.1	.4	6	8
112	9.1	10	20.4	5	5.0	2	3.5	1.3	17	25
98	9.3	11	25.5	12	7.1	12	3.7	1.5	14	21
101	9.5	12	27.2	13	9.5	14	1.2	.9	4	10
110	9.6	13	25.3	11	5.8	6	5.6	1.7	22	29
25	10.8	14	38.7	14	9.0	13	3.6	1.3	9	14
33	11.7	15	49.3	15	14.6	15	4.4	2.2	9	15
		Average	24.7		6.8		2.9	1.1	10	14
Spread among ave. fabric stiffness values, σ_a			8.6		2.6					
Relative spread, $\frac{\sigma_a}{\text{ave.}}$ (100)			.35		.38					
Discrimination Sensitivity Index, $\frac{\sigma_a^2}{\bar{\sigma}_w^2}$			9		6					

Relationships

Rank correlation with weight: T.O., .82; P, .52
Equation relating stiffness measurements on the two testers: T.O. = 3.4 + 3.1 P
Correlation (r) between T.O. and Peirce = .93

however, that the Tinius Olsen values are more closely related to the weight of the fabric than are the Peirce values. This is shown by the rank correlation coefficient between Tinius Olsen stiffness values and weight—namely, 0.82 as against 0.52 for the Peirce.

Reproducibility

Both the standard deviation, σ_w, and the coefficient of variation, V, of the ten stiffness measurements for each fabric were used as the basis for evaluating the precision or reproducibility of each machine. On the average, the standard deviation, σ_w, of the Tinius Olsen measurements is almost three times as large as for the Peirce measurements, but the coefficients of variation are approximately equal. This shows that there is little difference between the two testers in their relative precision or spread (in percent) of the readings for each fabric about its average stiffness value.

Sensitivity

An analogous situation exists in the spread of the average stiffness values of the fifteen fabrics. The standard deviation of the Tinius Olsen average stiffness values is approximately three times that of the Peirce, but the relative spread of the two machines—spread in relation to the average of the fifteen values—is about the same.

Sensitivity Index

The sensitivity index takes cognizance of the spread of the average stiffness values of the fifteen fabrics as evaluated by the standard deviation of their averages, σ_a; and the reproducibility among the specimen stiffness values for any one fabric as shown by their over-all average standard deviation, $\bar{\sigma}_w$. The ratio $\sigma^2_a/\bar{\sigma}^2_w$ is the sensitivity index; the higher the value, the better the discrimination. The indices of 9 and 6,

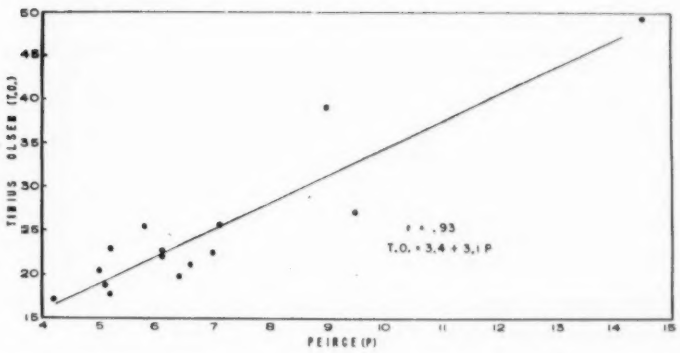

FIG. 3. *Relationship between stiffness values (in.= lb. × 10^{-4}) obtained on the Tinius Olsen and Peirce stiffness testers.*

TABLE II. STIFFNESS VALUES (10^{-4} IN.-LB.) OBTAINED ON THE TINIUS OLSEN AND PEIRCE STIFFNESS TESTERS BY 3 OPERATORS (5 SPECIMENS OF EACH OF 4 FABRICS)

	Tinius Olsen operators						Peirce operators					
	I		*II*		*III*		*I*		*II*		*III*	
Material	Amount	Rank	Amount	Rank	Amount	Rank	Amount	Rank	Amount	Rank	Amount	Rank
33	54	4	60	4	59	4	14.6	4	16.1	4	13.2	4
25	39	3	42	3	40	3	8.3	2	8.0	3	7.4	2
101	28	2	29	2	29	2	8.7	3	7.7	2	8.1	3
31	23	1	24	1	24	1	5.5	1	5.5	1	5.2	1
Operator ave.	36.0		38.8		38.0		9.3		9.3		8.5	
Inherent reproducibility (operator's ave. of 5 specimens)			10%						14%			
Over-all reproducibility (95% probability) (estimated max. % difference of any one operator average (5 specimens) from over-all fabric average)			13%						15%			

respectively, for the Tinius Olsen and Peirce machines, not being statistically different, indicate that both machines discriminate equally well among fabrics of differing stiffness.

Influence of Operators

Another problem is to determine whether there are any significant differences in stiffness values when different operators use each machine. Three operators evaluated five specimens of each of four fabrics, representing a wide range in stiffness and weight, on both the Tinius Olsen and Peirce stiffness testers. The results are shown in Table II. All four materials are ranked similarly by each operator on the Tinius Olsen, while there is a reversal of fabrics 25 and 101 by operators *I* and *II* on the Peirce tester. However, there is not a significant difference between the stiffness values of these two as measured by the Peirce apparatus.

Table II also shows the reproducibility on each tester of an average fabric stiffness value obtained by any one operator. It reveals the operator's precision and his ability to reproduce his own results. Any operator can be expected to come within 10% of his over-all fabric average 95% of the time when using the Tinius Olsen tester, and 14% on the Peirce tester.

The over-all reproducibility of the two testers is also shown in Table II. This is actually the measure of the dependability of the test method. It includes the two major sources of variability—inherent operator variability and differences between operators—and tells how much an operator's average of five specimens may deviate from the over-all fabric average 95% of the time. The Peirce averages can be expected to differ at most by 15%, and the Tinius Olsen averages by 13%.

Other Factors

Considering further advantages and disadvantages of the two machines, we find that the Tinius Olsen can measure a wider range of stiffnesses in fabrics than the Peirce tester in its present form. The

TABLE III. MINUTES REQUIRED TO OBTAIN STIFFNESS MEASUREMENTS ON TINIUS OLSEN AND PEIRCE INSTRUMENTS

Sample	Tinius Olsen	Peirce
11	1.68	0.33
25	1.87	0.32
33	1.60	0.30
31	1.65	0.28
101	1.68	0.30
	$\bar{X}$ 1.70	$\bar{X}$ 0.31

Peirce tester is limited to those fabrics which can bend under their weight to an angle of 43°. Therefore, a fabric rigid enough to support its own weight when projected as a cantilever for 6 in. could not be measured on the Peirce tester, while it could be bent on the Tinius Olsen to a moment weight up to 1 lb.

A disadvantage of the Tinius Olsen is that it is susceptible to mechanical failure or misfunction, unlike the far simpler Peirce instrument. Cases in the laboratory are on record where friction between the pendulum and the outside case of the instrument have influenced and invalidated stiffness measurements. A check of the machine must be made before each sample is tested; and repairs are likely to be needed from time to time.

Furthermore, the Peirce tester is much easier to operate and is much faster than the Tinius Olsen tester. Table III shows the results of a time study on the two instruments, using five of the fabrics previously tested.

The time recorded included the time necessary to place the sample in the apparatus, test it, and remove it from the instrument. The average results of all five samples showed that a sample can be measured on the Peirce tester in roughly $\frac{1}{4}$th the time it takes on the Tinius Olsen instrument.

Summary

1. Stiffness values obtained on the Peirce stiffness tester are highly correlated ($r = 0.93$) with those of the Tinius Olsen tester, and are equally reliable.

2. Tinius Olsen stiffness values can be estimated from the Peirce values by the relationship T.O. = 3.4 + 3.1 P.

3. Both machines should discriminate equally well among fabrics of differing stiffness.

4. Any one operator's average stiffness value (of five specimens) should not deviate by more than 15% from the over-all average stiffness value (95% probability) obtained on either the Tinius Olsen or Peirce stiffness testers.

5. The Peirce is roughly six times as fast as the Tinius Olsen apparatus.

6. While the Peirce is a simpler machine and is easier to operate, its usefulness is limited by the fact that it cannot measure the wide range of stiffnesses of military fabrics.

Acknowledgment

In connection with this work, the help and suggestions of Mr. Louis I. Weiner, Chief, Textile Materials Engineering Laboratory, Quartermaster Research & Development Laboratories, are acknowledged with gratitude. Appreciation is also expressed to Mr. Stanley Backer, Quartermaster Corps Consultant, and to Dr. Milton Platt, Fabric Research Laboratories, Inc., for their review of this paper, and to Dr. Oscar Mandel of the Quartermaster Research and Development Laboratories for his editorial assistance. For his support of this program and for permission to publish this paper, the authors are indebted to Dr. S. J. Kennedy, Research Director for Textiles, Clothing and Footwear, Office of The Quartermaster General.

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(Manuscript received March 16, 1953.)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the Journal. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the Journal is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Auto-hydrolysis of Jute Hemicellulose

Indian Central Jute Committee
Technological Research Laboratories
Calcutta, India
June 22, 1953

To the Editor
Textile Research Journal

Dear Sir:

In a previous communication from these Laboratories * it was stated that the highest yield of reducing sugar, calculated as xylose, obtained by the hydrolysis of hemicellulose I from jute with dilute sulfuric acid was 79.4%. The theoretical value, on the basis that the methylaldobiuronic acid does not exhibit full reducing power towards Fehling solution, was calculated to be 85.5%. Both mineral acids and strong organic acids partially decompose xylose even in dilute solution at boiling temperature. Since ash-free hemicellulose I behaves as a moderately strong acid (having pH 2.6 in aqueous solution), a 0.5% solution of it in boiled-out distilled water was heated under reflux and the amounts of reducing sugar set free (only xylose was detected in the hydrolyzate by paper chromatography) were estimated at regular intervals. The solution turned brown, and traces of furfural could be detected with aniline acetate. The highest yield of sugar was 83.6%, as shown in Table I.

TABLE I

Time (hrs.)	Reducing sugar as xylose (%)
24	12.5
48	30.9
72	43.5
96	50.5
120	57.8
144	63.2
168	66.9
192	69.2
216	72.5
240	74.6
264	77.5
288	79.3
312	83.5
384	83.6

A. K. Mazumdar
P. B. Sarkar

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INDUSTRIAL SECTION

New Roving Twist Formula

J. R. Corley, J. Simpson, L. A. Fiori, and J. J. Brown

Southern Regional Research Laboratory, New Orleans, Louisiana*

Introduction

It is known that spinning performance is largely dependent upon properly twisted roving. Manufacturers have customarily used staple length alone as the one fiber property to determine the amount of twist to insert, no doubt because length is the chief criterion in buying and selling cotton. Another reason for using staple length as the only important factor controlling twist has been that, while fineness was known to be an important property, it was believed to be generally so closely correlated with length that length was the only fiber property used in calculating twist. The fallacy of this belief was not established until adequate facilities became available for determining the independent relationship between fiber fineness and twist.

The oldest roving twist formula on record, whose origin is unknown, is based on the premise that twist is proportionate to the square root of the hank (size) roving. This formula does not take staple length into account and is applicable over only a limited range of hank rovings. The formulas of Bissonnette [2], Brandt [3], Duerst [4], and Lawton [7] are based on both length and hank roving as factors influencing twist. However, twist determined by formulas based on these two factors does not give the same drafting qualities for all rovings, particularly when produced from cottons of different finenesses. Hayes [6] recognized the effect that fiber fineness and staple length have on roving twist, but did not propose a formula for calculating twist.

The importance of fiber fineness as one of the factors influencing twist was definitely established in a study at the Southern Regional Research Laboratory [5] on the relation of fiber fineness to single yarn properties. This work showed that when coarse and fine fibers of equal length were processed into equivalent hank rovings, the coarse fibers required more twist than the fine fibers. This study indicated that the inability to predict reliably the spinning performance of roving may have been due mainly to the failure to take fiber fineness, as well as length and hank roving, into consideration in determining the twist required for optimum processing results. Studies were initiated, therefore, at this Laboratory to develop a formula for determining roving twist which would take into account these three important variables—fiber fineness, staple length, and hank roving. The method of determining separately the relation of the three variables to twist and the development of a new roving twist formula based on these relationships are described here. This formula and the use of instrument measurements of fiber fineness should enable manufacturers to calculate the twist required to obtain more precisely the same drafting qualities for all rovings irrespective of hank (size), fiber fineness, or staple length.

Procedures for Obtaining Basic Data

To derive a formula incorporating the effect of the three factors which influence the amount of twist required to secure optimum processing results, it was necessary to obtain basic data on each. Obviously, it was essential to study cottons having as the variable only the fiber property to be evaluated, holding all other properties constant.

Fineness Data

The data needed to determine the relationship between fiber fineness and twist were available from

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I. Fiber Properties of Cut Cottons [5]

Fiber properties	Cotton varieties: Fineness experiment* Seaberry Sea Island	Mesa Acala	Tanguis	Rowden 41-B	Length experiment† S×P			
Lot numbers	1	2	3	4	5	6	7	8
Micronaire fineness [1b], curvilinear scale	3.1	3.8	4.6	5.4	3.8	3.7	3.7	3.8
Fibrograph [1a] upper-half mean length (in.)	.95	.93	.91	.90	.95	1.02	1.13	1.25
Mean length (in.)	.73	.72	.71	.72	.77	.77	.84	.95
Uniformity (ratio)	.77	.77	.78	.80	.76	.76	.74	.76
Maturity [1a] (%)	75	88	88	87	88	89	89	88
Tensile strength from Pressley index [1a] (1000 lbs./sq. in.)	79.3	78.9	77.6	80.5	89.6	88.3	88.8	87.7

* Cut to obtain a common mean length, with fineness as a variable.
† Cut to obtain a common fineness, with upper-half mean length as a variable.

the previous work on fiber fineness [5]. That investigation had been conducted on four cottons of different degrees of fineness but having all other important fiber properties approximately equal. To hold length constant, since length is almost inseparable from fineness, a special cutting technique was used whereby the four cottons were cut to a common mean length, which in this case was 72 in. (Fibrograph*). Table I, under "fineness experiment," shows the fiber properties of the four cut cottons. These cottons were processed into a series of rovings ranging from 1.3 to 4 hank on appropriate types of long draft roving systems—10 in. × 5 in. Interdraft or 8 in. × 4 in. Superdraft.

Length Data

The basic data on length were obtained in a study now in progress at this Laboratory to determine the effect of fiber length on yarn properties and processing techniques, a parallel study to that reported on fiber fineness [5]. In the length study, a long, fine-fibered cotton (S × P) was used. This cotton was cut to upper-half mean lengths (Fibrograph) of .95, 1.02, 1.13 and 1.25 in. Obviously, since only one lot of one variety was used, fineness and the other fiber properties were constant in each of the samples which had been cut to four different upper-half mean lengths. Table I, under "length experiment," shows the fiber properties of these cottons. The samples of the different lengths were processed into a series of rovings ranging from 0.5 to 6.6 hank on appropriate types of long draft systems, as were used in the fineness experiment.

* The mention of trade products does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

Hank Roving Data

A Deltapine cotton was used for relating hank roving to twist because it is widely grown and representative of the medium-staple varieties. The fiber properties of this cotton also provided the means for adjusting the fineness, length, and twist relationships developed from cut cottons to an uncut cotton basis. The average fineness and length measurements of this cotton were 4.3 Micronaire fineness (curvilinear scale) and $1\frac{1}{32}$ in. (classer's length). Rovings ranging from 0.5 to 6.00 hank were processed from this cotton on appropriate types of long draft roving systems, as were used for the fineness and length experiments. The 6.00 and 8.00 hank rovings were also processed on a 7 in. × 3 in. conventional draft roving frame.

Testing Procedures

The amount of twist to be inserted in manufacturing the rovings in the three experiments was determined on the Belger roving tester. The twist for each roving was arbitrarily considered most satisfactory when the recording on the tester chart was centered along the middle line of the range for medium twist. All fiber properties were determined in accordance with test procedures as outlined by the American Society for Testing Materials [1] in a standard atmosphere of 70° ± 2°F and 65 ± 2% R.H.

Method of Derivation

The existing relationships between twist and the variables fiber fineness, length, and hank roving were derived by plotting hank rovings of the previously described groups against the twists found to

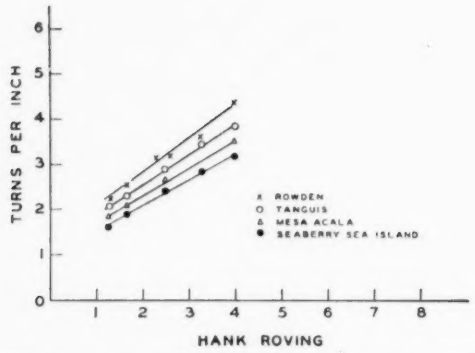

FIG. 1. *The effect of fiber fineness on turns per inch in roving.*

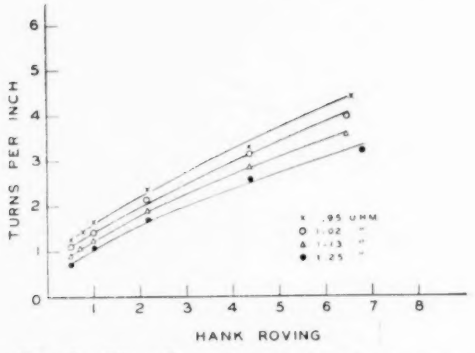

FIG. 2. *The effect of staple length on turns per inch in roving.*

yield the most satisfactory rovings. In plotting hank roving *vs.* twist, the resulting curves obtained were found to be of the type:

$$Y = K_1 X^n, \tag{1}$$

where Y = turn of twist per inch, X = hank roving, K_1 = a constant, and n = a constant. The value K_1 is constant for any one cotton, but differs with cottons of different lengths or finenesses.

Relation of Fineness to Twist

When the hank rovings manufactured from the four cottons used in the fineness experiments were plotted against the turns per inch required to obtain the same twist hardness, the resulting lines (Figure 1) showed that the rovings produced from coarse fibers required more twist than equivalent rovings from fine fibers. The calculated slopes of these lines were found to vary approximately as the square root of the Micronaire fineness (curvilinear scale), and it was assumed that the turns of twist followed a relationship of the type

$$Y = K_2(F)^{1/2}, \tag{2}$$

where F = fineness and K_2 = a constant.

Relation of Length to Twist

When the hank rovings, processed from the four cut lengths of S × P cotton, were plotted against turns per inch required to give the same twist hardness, it was found that rovings made from the longer lengths required less twist than those made from the shorter lengths—a relationship that is well known. It was found that the slopes of the resulting curves (Figure 2) at any given hank roving varied approximately inversely as the upper-half mean length (Fibrograph) or followed a relationship of the type

$$Y = \frac{K_3}{L}, \tag{3}$$

where L = U.H.M. length and K_3 = a constant.

Relation of Hank Roving to Twist

In order to determine the value of the exponent n in equation (1), the hank rovings processed from the uncut Deltapine cotton previously described were plotted against turns per inch (Figure 3). It was found that the value $n = 2/3$ gave a very close fit to the data, or $Y = K_1 X^{2/3}$.

Since the turns per inch required to produce satisfactory rovings from cottons were found to vary (*1*)

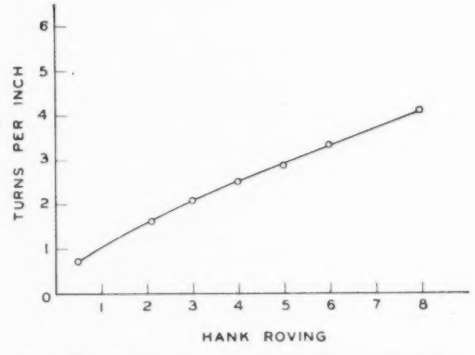

FIG. 3. *The effect of hank roving on turns per inch in roving.*

directly as the square root of fineness, (*2*) inversely as length, and (*3*) directly as (hank roving)$^{2/3}$, these relationships were expressed in the following general equation:

$$Y = \frac{K(F)^{\frac{1}{2}}(X)^{\frac{2}{3}}}{L}. \quad (4)$$

The value K was determined for equation (4) by substituting values of hank rovings for X and their corresponding values for Y from Figure 3 and the fiber properties of the Deltapine cotton fineness (4.3) for F and the classer's length (1.03) for L as follows:

$$K = \frac{(L)(Y)}{(F)^{\frac{1}{2}}(X)^{\frac{2}{3}}} = \frac{(1.03)(4.00)}{(4.3)^{\frac{1}{2}}(8.00)^{\frac{2}{3}}} = .498 \text{ or } .50. \quad (5)$$

Then the general equation for all cottons becomes

$$Y = \frac{.50(F)^{\frac{1}{2}}(X)^{\frac{2}{3}}}{L}. \quad (6)$$

This formula takes into account the effect that fiber fineness, staple length, and hank roving have on the twist required in roving, and provides a method of calculating roving twist to give more precisely the same drafting qualities for all rovings irrespective of hank roving, fiber fineness, and staple length of the cotton.

It was possible to substitute classer's length for U.H.M. in the formula, because of the good agreement existing between these values for the cottons used at this Laboratory. However, since the agreement between U.H.M. and classer's length of cottons may change [9] for various reasons, it would not always be advisable to substitute one for the other.

This formula is presented as a guide for determining the roving twists required to obtain maximum drafting efficiency for cottons varying widely in fiber

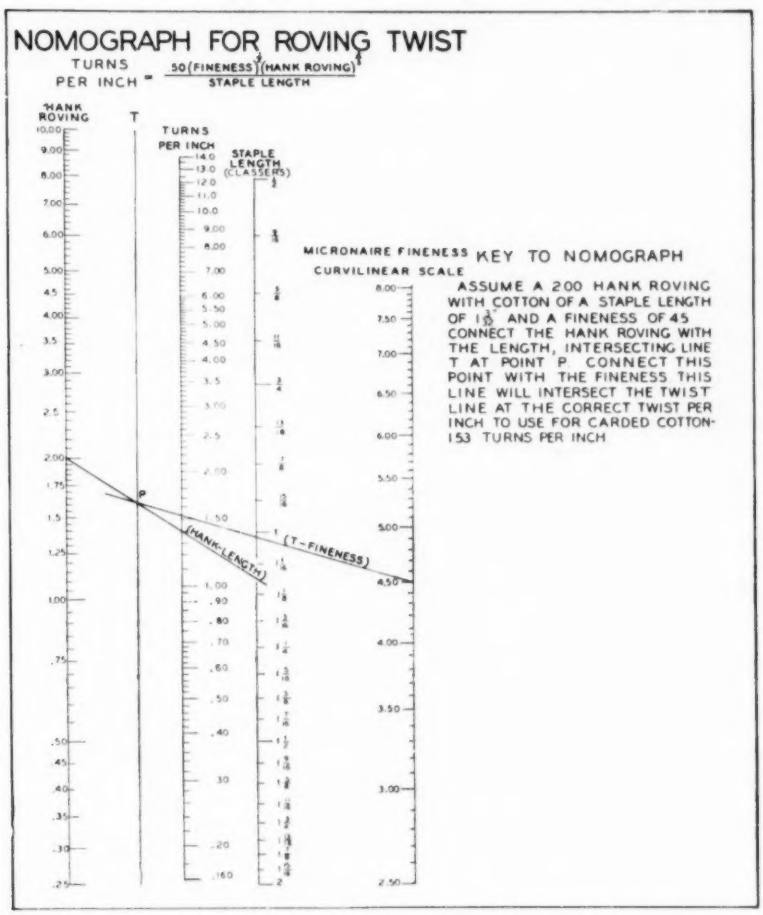
NOMOGRAPH FOR ROVING TWIST
TURNS PER INCH = 50(FINENESS)$^{\frac{1}{2}}$(HANK ROVING)$^{\frac{2}{3}}$ / STAPLE LENGTH
HANK ROVING
T
TURNS PER INCH
STAPLE LENGTH (CLASSER'S)
MICRONAIRE FINENESS
CURVILINEAR SCALE
KEY TO NOMOGRAPH
ASSUME A 200 HANK ROVING WITH COTTON OF A STAPLE LENGTH OF 1 3/32" AND A FINENESS OF 45 CONNECT THE HANK ROVING WITH THE LENGTH, INTERSECTING LINE T AT POINT P. CONNECT THIS POINT WITH THE FINENESS THIS LINE WILL INTERSECT THE TWIST LINE AT THE CORRECT TWIST PER INCH TO USE FOR CARDED COTTON- 153 TURNS PER INCH
P
(HANK-LENGTH)
(T-FINENESS)

FIG. 4. *Nomograph for determining turns per inch in roving when the fineness, length, and hank roving of a cotton are known.*

properties. It is fully recognized, however, that individual processing conditions such as levels of laboratory and classer's determinations and types of stock used (combed, dyed, etc.) may require some adjustment, because these factors may alter the values of the constants K and n. The proper value of the constant n for any individual condition can be determined by plotting hank rovings against the turns per inch required to give the correct twist in a manner similar to that shown for Deltapine cotton in Figure 3, and then calculating the equation of the resultant curve. The proper value for the constant K can be found by substituting the new value for the constant n and solving for K in a similar manner to that followed in formula (5).

A nomograph (Figure 4) based on the formula was constructed by means of standard construction techniques [8]. This nomograph enables rapid determination of the turns per inch of twist required in rovings ranging from 0.25 to 10 hank (size) from carded cottons varying widely in fiber fineness and length when the Micronaire fineness and classer's length are known.

Practical Applications

The new formula has been used for more than 18 months to calculate the required twist to insert in rovings processed at the Southern Regional Research Laboratory from carded cottons. The cottons used ranged from 2.4 to 7.1 Micronaire fineness (curvilinear scale), and from $\frac{3}{4}\frac{1}{2}$ to 2 in. (classer's length). During this time, rovings ranging from .5 to 10.00 hank produced with twist calculated by this formula have shown a uniform level of drafting qualities, irrespective of the fiber properties.

Mills measuring fiber fineness should be able to calculate with greater accuracy the twist required to give the desired twist hardness (drafting quality) for all rovings. The insertion of the proper twist in roving should eliminate to a great extent nonuniform yarn caused by overtwisted and undertwisted roving, and should result in fewer ends down during spinning and better operating efficiency throughout subsequent stages of manufacture.

Nomographs (size 8 in. × $10\frac{1}{2}$ in.) are available, without charge, from the Southern Regional Research Laboratory, 2100 Robert E. Lee Blvd., New Orleans 19, Louisiana.

Acknowledgments

The authors wish to express sincere thanks and gratitude to fellow staff members of the Cotton Mechanical Processing Division for processing the cottons into rovings and making the twist determinations; to Annie B. Cooper and Dorothy C. Legendre and coworkers of the testing section of the Analytical Division for fiber property determinations; and to K. Baringer for help in editing the manuscript. Without the help of these associates, this study would not have been possible.

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(*Manuscript received June 15, 1953.*)

Study on Picker Performance

Billy K. Power, Jack D. Towery, and Lyle E. Hessler

Cotton Research, Texas Technological College, Lubbock, Texas*

Abstract

An instrument is described for measuring the uniformity of picker laps and studying the performance of the pedal-type evener device. Studies indicate that the performance of the evener is reasonably good as a yard-to-yard evening device, but less effective for within-yard variations.

FORMATION of the picker lap offers the first opportunity for linear density control in the machine processes of cotton yarn manufacturing. The imperfections in the lap may be reflected in subsequent operations. Basically, the picker has remained essentially the same since its conception in the last century. With all the modern improvements made in yarn manufacturing machinery, the picker remains the only process incorporating an evening device for controlling the uniformity of stock. This evening device, which in the language of the modern engineer might be called a "mechanical" servo-mechanism, has been accomplishing its original purpose (yard-to-yard evenness) through these many years to the satisfaction of most mills. The question arises as to what happens in regard to variation within a yard of lap and its significance on subsequent operations.

The Instrument

Since the evener pedals with their associated linkages integrate the average thickness of the stock being fed, it is only necessary to record this movement for a study of variation in stock being fed prior to any evening action. A differential transformer was chosen for the displacement transducer because of its accuracy and adaptability [3]. The output from the pickup differential transformer, shown in Figure 1, is connected to a similar transformer in the recorder in a null balance system [4]. Such an arrangement gives freedom from line-voltage fluctuations. In Figure 2 is shown a schematic diagram of this arrangement. The recorder incorporates two differential transformers of different sensitivities, with their cores tandomly connected as pictured in Figure 3.† By means of a switch two different ranges are instantly available for maximum utilization of transformer output. Correspondent accuracies of 0.0005 in. for a core movement (integrated pedal movement) of 0.1

† The recorder was built to this specification by Schaevitz Engineering, Pennsauken Twp., Camden, N. J.

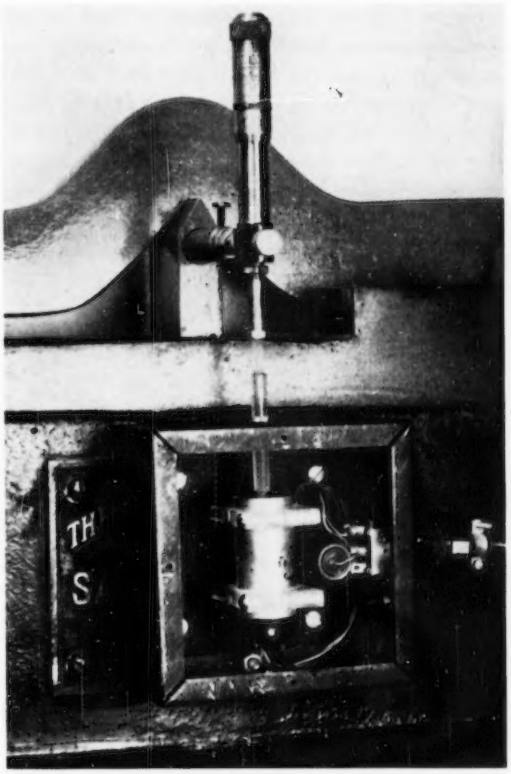

FIG. 1. *View of pickup differential transformer mounted on evener.*

* Fiber and Spinning Laboratory of The Cotton Research Committee of Texas.

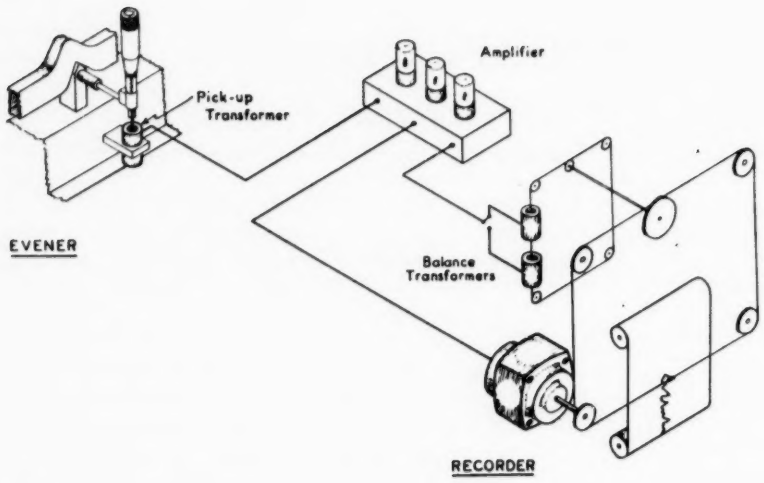

FIG. 2. *Schematic diagram of recorder system.*

in. is obtained. A core movement of 0.1 in. corresponds to 10 in. of pen travel on the chart.

Figure 4 shows the relationship between the average thickness as measured by the instrument and the weight per yard of lap. The regression of thickness to weight can be shown to be highly significant by analysis of variance. With a load on the pedals to give an average density of 14 lbs./ft.^{3} an apparent curvilinear trend can be noted beyond a lap weight of 13 oz. Increasing the load on the evener pedals extends the linear relationship between thickness and weight. Laps used in this study were from 8 to 12 oz./yd. No difference in density with a given load was evident for cotton of 3.5 to 4.8 μg./in. fineness as measured by the Micronaire.

Procedure

The measurements of variation were made by attaching the pickup differential transformer to the evener pedal lever, as shown in Figure 1. This enabled measurements of variation in stock thickness to be made prior to lap formation at the screen and calender-roll sections. The picker was a convential two-beater, one-process picker equipped with Aldrich rotary blade and Kirschner beaters. The evener motion was a Perham-Davis top tripod type.

In order to measure the variation in thickness of the finished lap, it was desirable to use a similar pedal motion with the same hookup as shown in Figure 1. This was accomplished by attaching a lattice apron to a calender-roll section with a total draft of 1.04. The measuring device was installed at the end of the lattice apron in line with the nip of the top calender rolls. The load necessary for the pedals could be obtained by adjusting the fulcrum lever, without external loading or linkages being necessary.

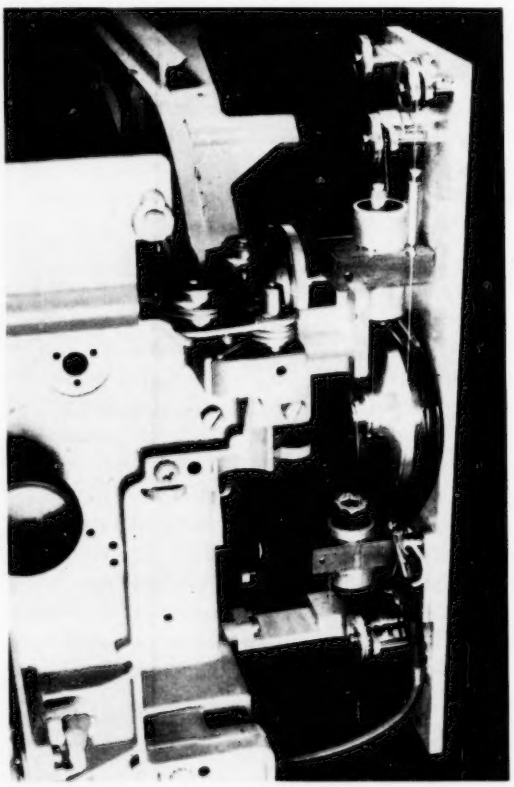

FIG. 3. *Tandomly mounted differential transformers of the recorder.*

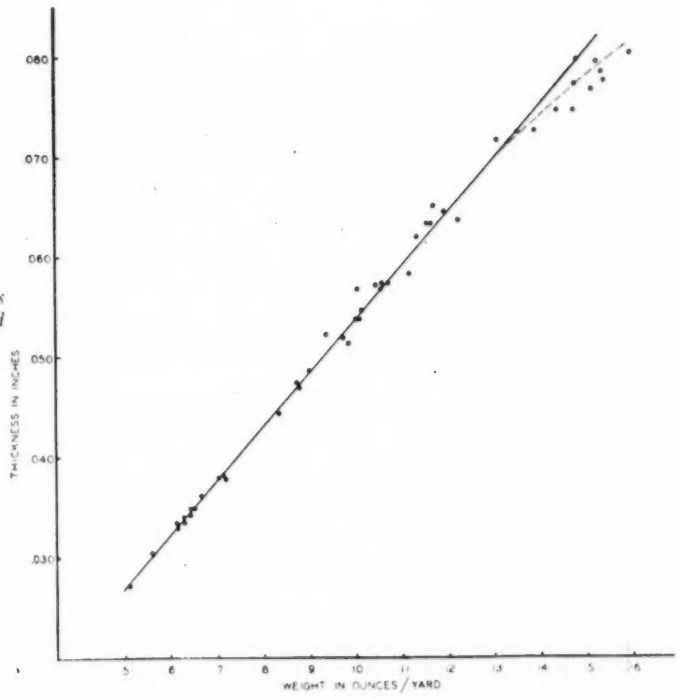

FIG. 4. *Relationship between thickness of lap and weight* ($y = .00538x$; *standard error of estimate* $= .0018$).

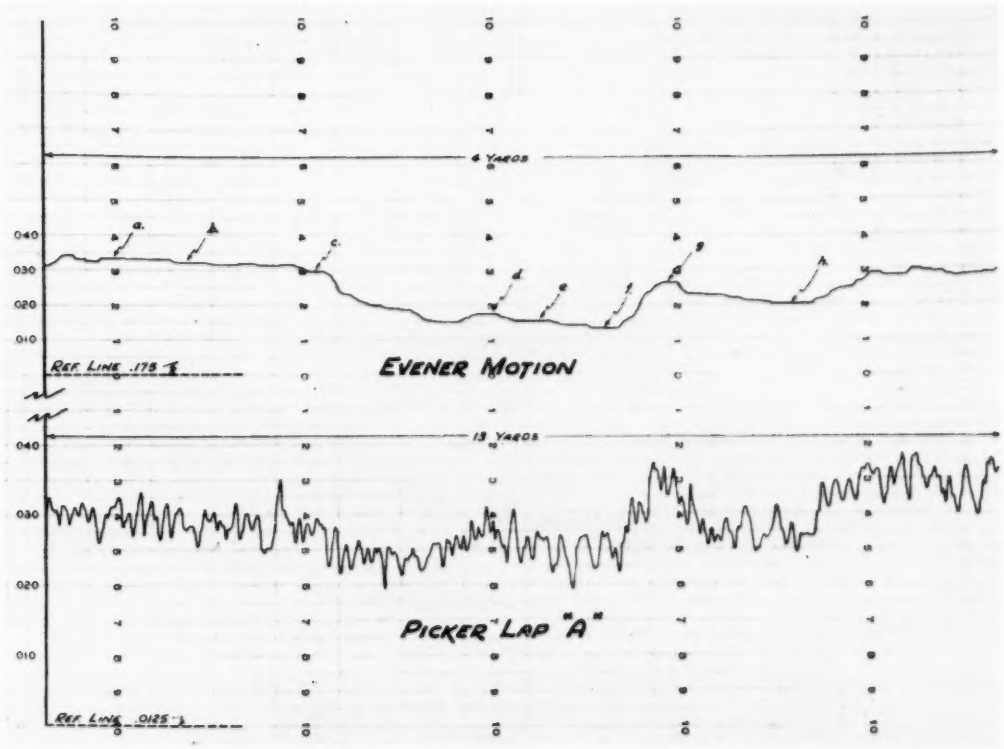

FIG. 5. *Portion of curves made of thickness of stock fed through the evener and after lap formation with evener disabled.*

Results

Evenness measurements made on the stock entering the evener prior to the beater and screen sections and after lap formation are shown in Figure 5 with the evener disabled, and in Figure 6 with the evener working normally. Lap *A*, made with the evener disabled, had a coefficient of variation of 7.8%, as compared with a coefficient of variation of 4.4% for lap *B*, made with the evener working normally. In order to have the same load applied to the evener pedals during both methods of operation, it is necessary to have all linkages including the belt shifting rack connected, because the friction and inertia effects of these are reflected back into the loading of the pedals. The flat places on the curves marked *a*, *b*, *c*, etc., in Figure 5 are due to such effects. These flat regions are absent when the linkage is disconnected from the lever arm, or they can be decreased at the expense of optimum lap uniformity by shifting the fulcrum so as to decrease the load on the pedals. The optimum position can only be determined by measuring the finished lap uniformity, because the compressional behavior of the cotton has its influence.

Evaluation of evenness from the charts was made by determining the coefficient of variation using a planimeter, and by computing the average maximum variation per unit length of chart. These methods express different qualities of the lap. In coefficient of variation all values for thickness are taken into consideration, and their dispersal is estimated with normal distribution. In average maximum variation per unit length, attention is directed to all the critical deviations in thickness. A chart with brief deflections of high amplitude may have a high average maximum variation, but a small coefficient of variation. A chart where the deflection is of a long wave nature, though not very high, may show a coefficient of variation that is large though the mean maximum variation is relatively small.

Much information on long-wave variations has

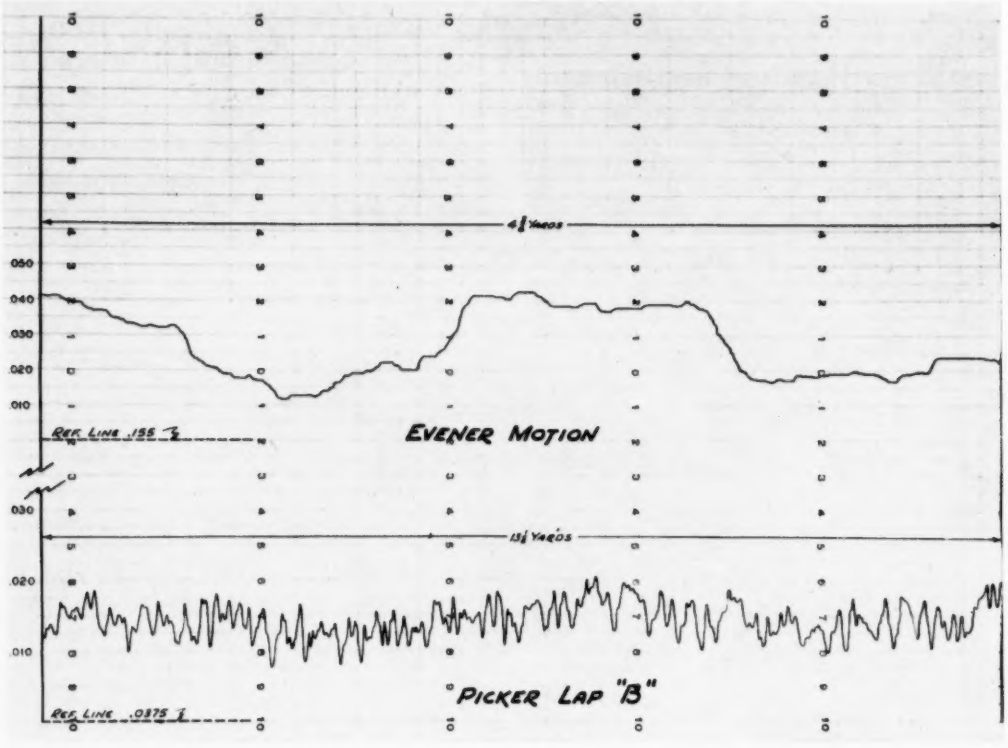

FIG. 6. *Portion of curves showing thickness of stock fed through the evener and after lap formation with evener working normally.*

TABLE I. Average Maximum Variation

Interval length (in.)	3	6	12	24	36
Lap *A*; evener not working	4.87	8.14	11.49	15.86	18.02
Lap *B*; evener working	4.88	8.01	11.29	13.56	14.63

been published. Attention here will be focused on the small-term variations (those occurring within a yard of lap) and the effect of the evener on these. Table I shows a comparison with and without the evener working while making the laps.

It is evident that this evener becomes most effective between lengths of 12 and 24 in. Variations of a shorter period than these apparently are the same for both laps produced by this picker. Since the evener indicates no measurable response to the short-term irregularities in a lap, it may be concluded that the factors affecting short-term variations appear to be acting independently of those affecting long-term variations. It is not difficult to conceive why two pickers may be producing laps of identical uniformity as measured on a yard-to-yard basis, and yet the slivers produced from these laps exhibit different uniformities.

Conclusions

The evener performs reasonably well as a yard-to-yard levelling device, with certain limitations. Friction and inertia influence response. Indications are that the thickness of the cotton in the range of loads impressed by the evener pedals for best control may not be linear. Since density is a function of load, the density was calculated from the measured thickness and known weight of the stock being fed to the evener. This density was from 16 to 18 lbs./ft.^{3} The thickness of a finished lap compressed to this density has been shown to be linear. The previous history of the cotton in a finished lap is entirely different, from a compressional behavior point of view, than the cotton passing under the evener pedals. Comparisons are not valid without more knowledge of the compressional behavior of the fiber.

The shortcomings of the present-day picker have not been overlooked. Koeb [2] made reference to an improved picker in dealing with the problems of unevenness in spinning. Kiselev [1] made recommendations for improvement in the operation of the pedal-type feed regulators.

If more uniform laps are to be made, from the standpoint of within-yard variation, then an evening device capable of greater sensitivity and rapid response needs to be developed. A device which measures the lap uniformity as it is being formed on the screens seems desirable, with control based upon aerodynamic principles. Possibly a screen or series of screens, each with individual sections and servo-controlled air pressures determining the amount of cotton deposited, could be designed. Provision should be made for any excess stock being returned to the screens as needed. The high productivity on the picker might make a more elaborate control mechanism economically justified. The ultimate in control in lap formation would be individual fiber control. The degree of success in reducing the size of the fiber aggregate without damage or nep formation remains to be explored.

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(*Manuscript received April 20, 1953.*)

Book Reviews

The Chemistry of Synthetic Dyes. Vols. I and II. K. Venkataraman. New York, Academic Press, Inc., 1952. Vol. I: 704 + xvi pages; price, $14.50. Vol. II: 1442 pages; price, $15.00.

(Reviewed by W. A. Raimond, Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.)

This is a comprehensive treatise, almost monumental, consisting of two volumes which include the chemistry of all known classes of synthetic dyes, with emphasis on the most important classes. Treatises such as this on the chemistry of synthetic dyes have been badly needed and eagerly awaited by those connected with the fields of research, manufacture, and application of dyes. The two volumes furnish excellent reference material not now available from any other single source.

Information on the synthesis of azo dyes, including mordant, metallized, resin-treated, pyrazolone types, as well as stilbene, thiazole, and azoic dyes, is given in Volume I. Diphenylmethanes, triphenylmethanes, xanthene acridine azines, oxazines, thiazines, quinones with different ring systems including anthraquinone dyes for cellulose acetate, for wool, cotton, and rayon, indigoid and thioindigoid dyes, soluble vats, sulfurs, phthococyanines, and cyanines are discussed in Volume II.

The author has placed particular emphasis on the two most important classes of synthetic dyes—namely, azo and vat dyes. Volume I is the best single book obtainable on the over-all subject of azo dyes. The references included are up-to-date, and the recent patent literature appears to have been well covered, along with the German literature. The chapters on the vat dyes include synthesis information on all of the commercially important vat dyes. The process information given is selective, and thorough literature surveys have evidently been made, particularly of the BIOS and FIAT reports.

In addition to the information on the synthesis of dyes, other information of more or less importance in a work of this type is included. The historical information on the dye industry and its commercial development is well done, well written, and deserves inclusion. Certain other subjects could have been omitted since they are not only not concerned with the synthesis of dyes, but contribute a number of pages without which it is possible that only one volume at a substantially lower cost could have been made available. Raw materials, including low-temperature carbonization, and the chapter on intermediates wherein sulfonation, halogenation, along with many individual compounds are discussed, most of which is information available in standard texts or handbooks, could well have been omitted. These chapters constitute practically an undergraduate organic chemistry text in themselves. The chapter on application of dyes could have been omitted along with its discussion of fibers, with no loss, and with some gain in brevity. Volume II is much superior in this respect, since it adheres more closely to the subject of dye chemistry and only veers off slightly to discuss the application of vat dyes and the constitution of cellulose.

Omissions are few in number, but further information on the optical bleaches or whitening agents, certified food dyes, and fast bases would have been desirable. A subject index included in Volume I would have been an improvement.

Considering the subject matter covered and the number of pages, there are surprisingly few typographical errors.

All in all, these volumes represent an excellent piece of work, although the author could have profited by F. M. Rowe's *The Development of the Chemistry of Commercial Synthetic Dyes* as an example of brevity and completeness.

Review of Textile Progress. Vol. III. Published jointly by The Textile Institute, Manchester, England, and the Society of Dyers and Colourists, Leeds, England. 1952. 590 pages. Price, 35/– ($5.00).

(Reviewed by J. H. Wakelin, Textile Research Institute, Princeton, N. J.)

Volume III of the *Review of Textile Progress* follows generally the same subject outline and format as the previous two volumes published in 1950 and 1951. In the present volume a detailed account is given of the scientific and technical literature in the field of textiles based principally on papers published during 1950 and 1951. This volume is the most extensive of the three and includes over 2,900 references to scientific publications and to British and American patents. The *Review* is well balanced in its presentation of results of scientific investigations and technological advances in production, processing,

and testing. The material covered includes the physics and chemistry of fibrous materials; fiber production; conversion of fibers into finished yarns; fabric production; coloring matters; coloring of textiles; finishing; analysis, testing, grading, and defects; laundering and dry cleaning; building and engineering; and industrial application of textiles. As stated in the "Introduction" to Volume III, a discussion of nylon has been added to the "Physics and Chemistry of Fibrous Materials," and the chapter on "Fabric Production" has been enlarged to include sections on "Sizing and Sizing Materials" and "Felt." The chapter on "Analysis, Testing, Grading and Defects" has been divided into two sections—one dealing with "Physical Testing" and the other with "Chemical Testing." A new chapter entitled "Industrial Applications of Textiles" has been added.

The *Review* is well documented and includes extensive name and subject indexes. It is certainly to be recommended as source and background material for the research worker as well as the practical mill man. The material in the *Review* is well written, well planned in subject coverage, and represents a well-coordinated effort on the part of the editors.

Two Thousand Years of Textiles. Adele Coulin Weibel. Published for the Detroit Institute of Arts. New York, Pantheon Books, 1952. 169 + ix pages + 256 plates. Price, $20.00.

Many are the reasons why so many persons are fascinated by the textiles which were designed and woven in the ages before the dawn of this era. They furnish clues to the culture of different periods, and the artistic skill displayed frequently coincides with the rise and decline of civilizations, as is true with other forms of art. Motifs employed in present-day decorative work—not only in textiles—are being copied from these fabrics, many of which are breathtakingly beautiful.

The study of old textiles has been complicated by the fact that they are widely scattered in museums throughout the world. One has to resort to numerous catalogues, pamphlets, and books, any one of which gives only a limited picture of the whole.

Here is a book, the first comprehensive work on textile art to be published in the English language, which presents a history of the development commencing with the fragments preserved in the Neolithic cave dwellings and bog burials. The major part is devoted to 256 plates, some in color, illustrating 331 fabrics, and including 95 pages of description of the fabrics, all arranged chronologically. The illustrations show the design on an unusually large scale. An introductory section discusses materials and techniques employed by the craftsmen, and a historical section describes the development in the principal areas of the world and reveals many of the customs of the periods and the influence of these on the arts. The pages are large (9 in. × 12 in.) and the book is attractively bound.

The author is a specialist in all branches of textile art: woven fabrics, embroidery, lace, rugs, and tapestry. This knowledge is based on a sound training in the history of art.

The Chemistry of Lignin. Friedrich Emil Brauns. New York, Academic Press Inc., 1952. xv + 808 pages. Price, $14.50.

(Reviewed by Joseph L. McCarthy, Professor, Department of Chemistry and Chemical Engineering, University of Washington, Seattle 5, Washington)

The appearance of the book *The Chemistry of Lignin* may be regarded as an important milestone in the march toward understanding of lignin as a polymeric phenol which makes up about one third or one fourth of the mass of the woody tissue of higher plants. This book has been prepared by Dr. F. E. Brauns, a serious and conservative scientist who for many years has been active in research to extend knowledge of lignin and other natural products.

Dr. Brauns was educated in the German universities. He conducted research with such men as Dr. Emil Fischer at Berlin and Dr. Karl Freudenberg at Munich, Freiberg, and now at Heidelberg. It was perhaps from these men that he received his initial inspiration to investigate the chemistry of natural products. After some industrial research experience in Germany, including a period of four years with Zellstoff-Fabrik Waldhof, Dr. Brauns came to Canada in 1930 where he carried out research on lignin as a coworker with Professor Harold Hibbert at McGill University in Montreal. In 1935 he became associated with the Institute of Paper Chemistry of Lawrence College at Appleton, Wisconsin and he has continued his work on lignin and carbohydrates at this institution down to the present time.

The Chemistry of Lignin deals with all aspects of the physical and chemical behavior of lignin. The organization and devolpment of the subject matter of the book is shown by recording the following key words roughly indicating the order and content of

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the twenty-seven chapters: History, definitions, distribution, color reactions, isolation and extraction, determination, physical properties, elementary composition and constituent groups, acylation and acylysis, alkylation, halogenation, nitration, sulfonation, hydrolysis, alcoholysis, mercaptolysis, phenolysis, hydrogenation and hydrogenolysis, oxidation, alkali fusion, special reactions, thermal decomposition, biological decomposition, theories on structure and linkages of lignin in the plant, theories of formation, and synthetic lignins.

The treatment of the subject matter has been to enumerate and describe briefly the experiments done and the results reported, largely from the viewpoint of the classical organic chemist. This has made the book very valuable in the handbook sense in that it comprises an organized compilation of the vast literature of this field. It appears that the author has had to face two major difficulties in working with this subject. First, very much practical and industrial development type study has been done on lignin and the author has had the task of selecting and recording the permanently significant facts and omitting those of only passing or timely interest. Second, there is not yet at hand a generally acceptable structural framework around which one can assemble the physical and chemical facts concerning lignin structure and reactions. This has meant the required reporting of experimental results in a semi-empirical way whereby some results then seem to be internally inconsistent. However, this situation seems to be inevitably associated with the still incompletely elucidated structure of lignin and the author has very capably presented the material so far available in this difficult field.

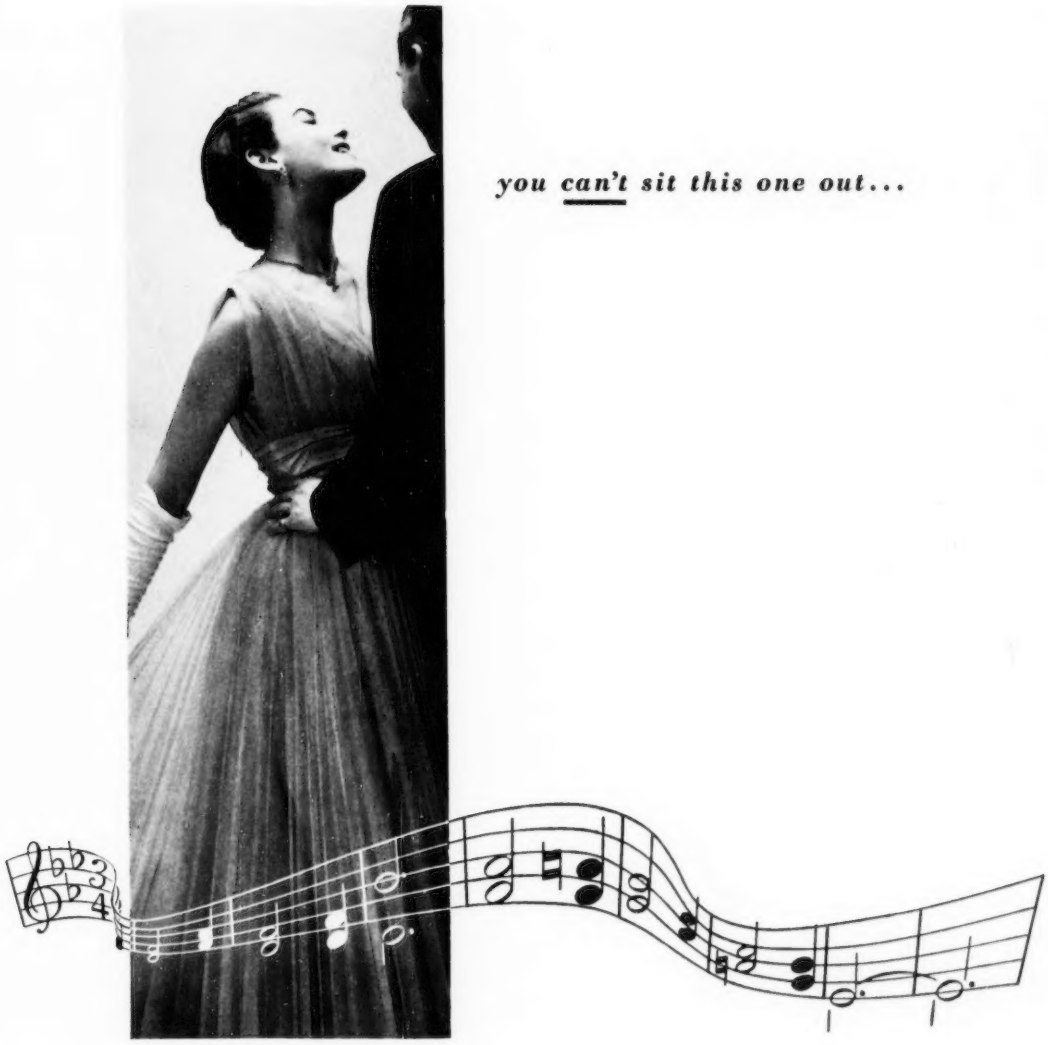
This important and valuable book will be of particular utility to persons engaged in research on the structure and reactions of lignin, and to those working to develop industrial processes for recovery or conversion of lignins to yield useful products. Although the book does not include special information on practical utilization of lignin, it will be of major importance as a source from which a chemist can rapidly obtain a detailed chemical background for interpretation of the results of the research and development which is steadily proceeding to evolve uses for the lignin available in sulfite waste liquor and other pulping by-product liquors, as well as the lignin in the unused wood of lumber mills and forests.

Maleic Anhydride Derivatives. Lawrence H. Flett and William Holett Gardner. New York, John Wiley & Sons, Inc., 1952. 269 pages. Price, $6.50.

(Reviewed by Hillary Robinette, Jr., Chemical Consultant, Ardmore, Pa.)

In 269 pages, the authors have presented a hundred and sixteen different types of chemical reactions involving Maleic Anhydride, or one of its simple unsaturated derivatives. The reaction is given whether it takes place with maleic acid, fumaric acid, their esters, amides, or other unsaturated derivatives.

The book is written using the unique style of a two-page monograph per reaction. On one page the chemistry of the reaction is illustrated with structural formulas, followed by a method of preparation of a type compound and selective references; on the facing page are given a discussion of the reaction, a description of properties of the chemical produced and discussions of uses.

The format of the book is designed so that one can locate most reactions merely by leafing through it. However, an excellent index and a table of contents have been provided. Students and research workers in synthetic organic chemistry will be happy to have this book available. It will prove to be an invaluable source of information for chemists seeking new compounds or methods to solve their problems.

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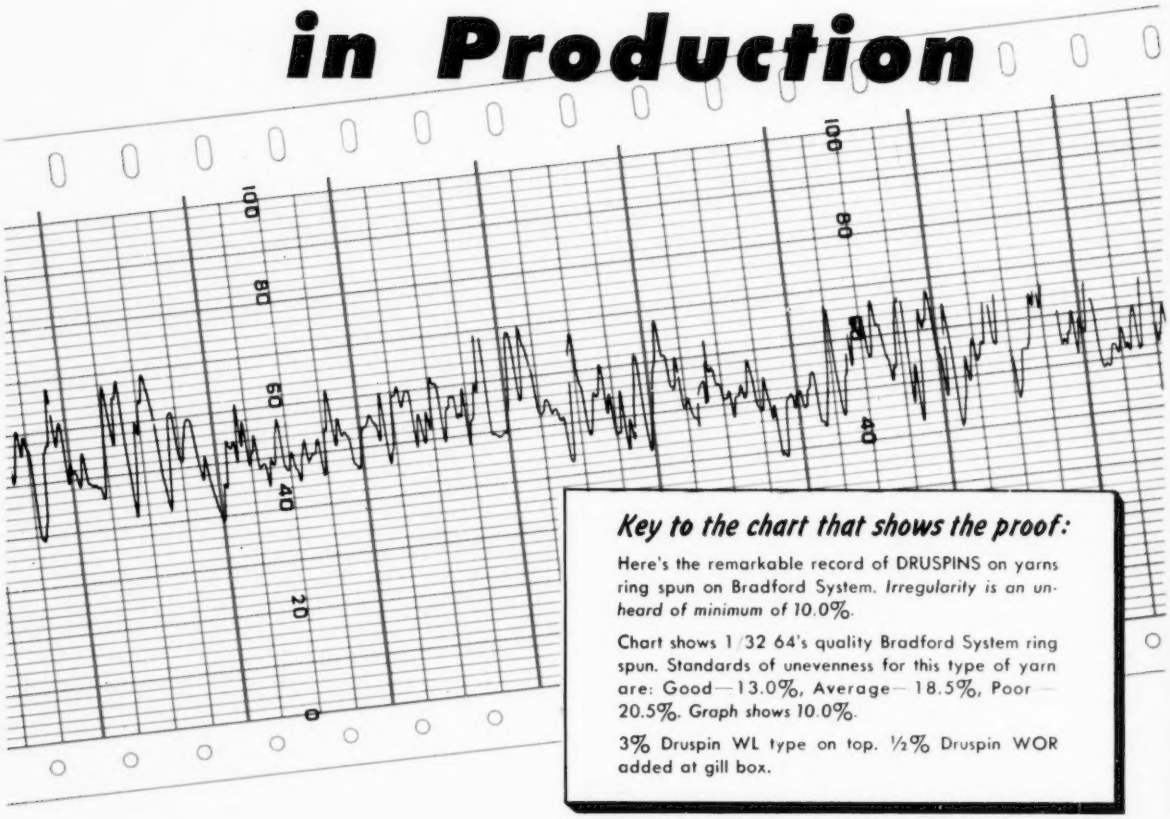

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